Conseil national de recherches
Canada
Institut de génie des
matériaux
Boucherville (Québec)

National Research Council
Canada
Industrial Materials
Research Institute
Boucherville, Quebec

PHYSICOCHEMICAL CHARACTERIZATION OF HIGH-PERFORMANCE FIBRE-REINFORCED ORGANIC-MATRIX COMPOSITES
PART 4. APPLICATIONS OF PYROLYSIS GAS CHROMATOGRAPHY AND THERMAL ANALYSIS

IGM87RT-101-535-G
CNRC 27369

PHYSICOCHEMICAL CHARACTERIZATION OF HIGH-PERFORMANCE FIBRE-REINFORCED ORGANIC-MATRIX COMPOSITES

PART 4. APPLICATIONS OF PYROLYSIS GAS CHROMATOGRAPHY AND THERMAL ANALYSIS

by

D. Noël, J.-J. Hechler, K.C. Cole

Industrial Materials Research Institute
National Research Council Canada
75, boul. de Mortagne
Boucherville, Québec, Canada
J4B 6Y4

January 1987

TABLE OF CONTENTS

List of figures....iv
List of tables....vi
Preface....vii
Acknowledgment....viii
Summary....ix
Résumé....x

1. PYROLYSIS - GAS CHROMATOGRAPHY....1

1.1 Introduction....1

1.2 Experimental Section....2
1.2.1 Pyrolysis - Capillary Gas Chromatography....2
1.2.2 Pyrolysis - Gas Chromatography - Fourier Transform Infrared Spectroscopy....3
1.2.3 Chemicals and Sample Preparation....3

1.3 Results and Discussion....4
1.3.1 Optimization of Pyrolysis Conditions....4
1.3.2 Pyrolysis of Prepregs....9
1.3.3 Pyrolysis - Gas Chromatography - Fourier Transform Infrared Spectroscopy....12
1.3.3.1 Optimization of the make-up gas....13
1.3.3.2 Pyrolysis with a capillary column coated with a film of thickness 0.25 µm....13
1.3.3.3 Pyrolysis with a capillary column coated with a film of thickness 5 µm....16
1.3.4 Quantitative Determination of the Hardener in the Epoxy Resin System..18
1.3.5 Curing of the Rigidite 5208/WC3000 Prepregs....19

1.4 Conclusions....20

2. THERMAL ANALYSIS....21

2.1 Introduction....21

2.2 Experimental Section....23
2.2.1 Materials....23
2.2.2 Thermogravimetric Analysis....24
2.2.3 Differential Scanning Calorimetry....24

2.3 Results and Discussion....25
2.3.1 Thermogravimetric Analysis....25
2.3.1.1 Nitrogen atmosphere....25
2.3.1.2 Oxygen atmosphere....27
2.3.1.3 Air atmosphere....41
2.3.2 Differential Scanning Calorimetry....43
2.3.2.1 Optimization....43
2.3.2.2 Comparison of different batches of Narmco 5208....48

2.4 Conclusions....50

TABLE OF CONTENTS (contd.)

3. RECOMMENDED METHODS.....51

3.1 Pyrolysis - Gas Chromatography.....51

3.2 Thermal Analysis.....51

4. REFERENCES.....53

LIST OF FIGURES

Figure	Description	Page
1	Dependence on the pyrolysis temperature of the percentage of residue and the relative area of the peaks eluting before 4 minutes for Rigidite 5208 epoxy resin.	5
2	Pyrogram of 4,4'-diaminodiphenylsulphone (DDS).	7
3	Variation of the peak area as a function of the sample mass for Rigidite 5208/WC3000 prepreg.	8
4	Pyrograms of Narmco 3203/WC3000 prepreg (A), Ferropreg CE306/281 prepreg (B), and Araldite 6010 epoxy resin (C).	10
5	Pyrograms of Rigidite 5208/WC3000 prepreg (A), Ferropreg CE-9000-2/281 prepreg (B), and Araldite MY 720 epoxy resin (C).	11
6	Variation of the peak intensity and the peak width at half-height as a function of the flow rate of the make-up gas for ethyl acetate.	14
7	Gram-Schmidt reconstruction for the pyrolysis - capillary gas chromatography of DDS. Column: DB-17, 30 m x 0.259 mm i.d., film thickness 0.25 µm.	15
8	Gram-Schmidt reconstruction for the PGC of Rigidite 5208 epoxy resin. Column: OV-101, 60 m x 0.40 mm i.d., film thickness 5 µm.	17
9	TG curve of Narmco 5208 neat epoxy resin. Gas: nitrogen; heating rate: 10°C/min; mass of resin: 22.4 mg.	26
10	TG curve of Narmco 5208 neat epoxy resin. Gas: oxygen; heating rate: 10°C/min; mass of resin: 32.6 mg.	28
11	Enlarged area of Figure 10.	29
12	TG curve of graphite fibres. Gas: oxygen; heating rate: 10°C/min; mass of fibres: 24.1 mg.	30
13	TG curve of Narmco 5208 prepreg. Gas: oxygen; heating rate: 10°C/min; mass of prepreg: 54.9 mg.	31
14	Isothermal TG curve of Narmco 5208 prepreg. Gas: oxygen; temperature: 500°C; mass of prepreg: 47.7 mg.	33
15	Isothermal TG curve of Narmco 5208 prepreg. Gas: oxygen; temperature: 460°C; mass of prepreg: 40.0 mg.	34
16	Isothermal TG curve of a prepared mixture of epoxy resin (65.2% w/w) and graphite fibres (34.8% w/w). Gas: oxygen; temperature: 420°C; mass of sample: 65.3 mg.	35

LIST OF FIGURES (contd.)

17	Enlarged area of Figure 16	36
18	TG curve of a prepared mixture of epoxy resin (40.3% w/w) and graphite fibres (59.7% w/w). Gas: oxygen; heating rate: 10°C/min; mass of sample: 37.7 mg.	38
19	Enlarged area of Figure 18.	39
20	Comparison of TG curves of the prepared mixture of epoxy resin and graphite fibres and of the Narmco 5208 prepreg.	40
21	TG curve of Narmco 5208 prepreg. Gas: air; heating rate: 10°C/min; mass of prepreg: 63.5 mg.	42
22	TG curve of Narmco 5208 prepreg. Gas: oxygen; heating rate: 10°C/min; mass of prepreg: 37.2 mg.	44
23	DSC curve of Narmco 5208 prepreg. Gas: oxygen; heating rate: 5°C/min.	45
24	TG curve of Narmco 5208 prepreg. Gas: nitrogen; heating rate: 10°C/min; mass of prepreg: 30.5 mg.	46
25	DSC curve of Narmco 5208 prepreg. Gas: nitrogen; heating rate: 5°C/min.	47

LIST OF TABLES

Table	Description	Page
1	Variation of the weight loss on pyrolysis as a function of the sample mass for Rigidite 5208/WC3000 prepreg.	9
2	Variation of the ratio of the aniline peak against the phenol peak as a function of the amount of DDS for different mixtures of DDS and TGDDM.	18
3	Ratio of some peaks of the pyrogram of Rigidite 5208/WC3000 prepreg against the aniline peak as a function of the curing temperature for a one-hour cure.	19
4	Thermogravimetric results obtained with known mixtures of epoxy resin and graphite fibres.	37
5	DSC results for different batches of Narmco/WC3000 prepreg.	48

PREFACE

This report is the fourth of a series resulting from a cooperative effort involving the Industrial Materials Research Institute (IMRI) of the National Research Council Canada (NRCC) (Boucherville, Québec) and Canadair Limited (Montréal, Québec). The subject is one of growing importance in high-technology manufacturing, namely the physicochemical characterization of high-performance fibre-reinforced organic-matrix composites. This report is divided into two main sections. The first describes the results of original research involving the application of pyrolysis - capillary gas chromatography to the graphite-epoxy system Narmco Rigidite 5208/WC3000. The second part gives results obtained on the same system but using differential scanning calorimetry and thermogravimetric analysis. Other reports include a literature review and descriptions of original research involving spectroscopic and liquid chromatographic techniques applied to a commercial composite. The titles of the complete series are as follows:

Part 1. General Discussion and Literature Review
Part 2. Applications of Infrared Spectroscopy
Part 3. Applications of Liquid Chromatography
Part 4. Applications of Pyrolysis - Gas Chromatography and Thermal Analysis
Part 5. A Study of the Room-Temperature Aging of Narmco 5208/WC3000 Prepreg
Part 6. Methods for Quality Control of Matrix Chemistry

ACKNOWLEDGEMENT

Apart from the authors, the following people directly contributed to the research described in this series of reports:

H. Roberge	NRCC-IMRI
A. Pilon	NRCC-IMRI
J. Boulanger	NRCC-IMRI
K.C. Overbury	Canadair Ltd.
A. Chouliotis	Canadair Ltd.
S. Toye	Canadair Ltd.

SUMMARY

The first part of this report describes the application of a pulse-mode pyrolysis technique coupled with capillary gas chromatography to characterize epoxy-based composites. The pyrolysis has been optimized with respect to the pyrolysis temperature and the sample mass in order to obtain reproducible quantitative results. Pyrolysis at 650°C for 10 seconds using a sample mass of less than 1 mg has been found to give a sufficient quantity of pyrolyzed material without producing too complex a mixture of pyrolysis products. Pyrolysis - capillary gas chromatography (PGC) has been used to determine the amount of hardener in an epoxy resin system by ratioing the aniline peak area against the phenol peak area. It has also been used to characterize different prepregs, and to evaluate the curing of an epoxy resin. Some pyrolysis products have been identified by coupling PGC with Fourier transform infrared spectroscopy. In this case, the use of an OV-101 capillary column with a film thickness of 5 μm allows the injection of a larger amount of pyrolyzed resin, thus improving the detection without loss of resolution.

In the second part of this report, a differential scanning calorimetry (DSC) method has been developed to characterize epoxy-graphite prepregs. DSC was done with nitrogen as the atmosphere in order to avoid the oxidation reactions which degrade the epoxy resin during heating. Since the resin distribution in a given batch of prepreg is not entirely uniform, and since the sample used for DSC is relatively small, the percentage of resin may vary significantly from sample to sample, even though they are taken from the same sheet of prepreg. Hence, the exact resin content must be determined for each sample in order to obtain reproducible values for the curing enthalpy. A thermogravimetric (TG) method using an oxidizing atmosphere has been developed for this purpose. After the DSC experiment, a TG analysis is done on the same sample. The exact mass of resin is found on the TG curve at the inflexion point corresponding to the end of oxidation of the epoxy resin and to the beginning of oxidation of the graphite fibres. For the Narmco 5208/WC3000 prepreg, this inflexion point is located at a temperature of about 565°C. This procedure gives enthalpy values with a relative standard deviation smaller than 1%.

RÉSUMÉ

Dans la première partie de ce rapport, la pyrolyse en mode pulsé a été couplée avec un chromatographe en phase gazeuse en utilisant une colonne capillaire pour caractériser des composites à base de résines époxydes. La pyrolyse a été optimisée par rapport à la température de pyrolyse et à la masse de l'échantillon de façon à obtenir des résultats quantitatifs reproductibles. Une pyrolyse de 650°C durant 10 secondes avec une masse d'échantillon inférieure à 1 mg donne une quantité suffisante de matières pyrolysées sans produire un mélange trop complexe de produits pyrolysés. La pyrolyse - chromatographie en phase gazeuse sur colonne capillaire a été utilisée pour déterminer la quantité de durcisseur dans un système de résine époxyde en calculant le rapport de la surface du pic de l'aniline sur la surface du pic du phénol. Cette technique a aussi été utilisée pour caractériser différents préimprégnés et pour évaluer le durcissement de la résine époxyde. Quelques produits de pyrolyse ont été identifiés par le couplage de la pyrolyse - chromatographie en phase gazeuse avec un spectrophotomètre infra-rouge à transformée de Fourier. Dans ce cas, l'utilisation d'une colonne capillaire OV-101 avec un film de 5 µm d'épaisseur a permis l'injection d'une plus grande quantité de résine pyrolysée afin d'améliorer la détection sans perte de résolution.

Dans la seconde partie de ce rapport, une méthode de calorimétrie différentielle à balayage (CDB) a été développée pour caractériser un composite à base de résine époxyde et de fibres de graphite. L'analyse a été réalisée avec une atmosphère d'azote dans le but d'éliminer les réactions d'oxydation qui dégradent la résine époxyde durant la montée en température. La répartition de la résine dans un lot particulier de préimprégné n'est pas complètement uniforme, et l'échantillon utilisé pour la CDB est relativement petit. Le pourcentage de résine peut donc varier d'un échantillon à l'autre même si ceux-ci proviennent de la même feuille de préimprégné. La quantité exacte de résine doit être déterminée pour chaque échantillon de façon à obtenir des valeurs reproductibles pour l'enthalpie de durcissement. A cet effet, une méthode thermogravimétrique employant une atmosphère oxydante a été développée. Après l'expérience de CDB, une analyse thermogravimétrique est réalisée sur le même échantillon. La masse exacte de résine est déterminée sur la courbe au point d'inflexion correspondant à la fin de l'oxydation de la résine époxyde et au début de l'oxydation des fibres de graphite. Pour le système Narmco 5208/WC3000, ce point d'inflexion est localisé à une température d'environ 565°C. Cette procédure permet d'obtenir des valeurs d'enthalpie avec un écart-type relatif inférieur à 1%.

1. PYROLYSIS - GAS CHROMATOGRAPHY

1.1 INTRODUCTION

In recent years, pyrolysis-gas chromatography (PGC) has undergone considerable growth as an analytical technique applied to the characterization of macromolecules. With the development of capillary columns, this technique has become extremely useful in the industrial research laboratory and in the polymer industry [1-3]. Pyrolysis overcomes the difficulty of analyzing high-molecular-weight compounds which are not volatile, such as plastics or paints. For example, PGC can detect methyl, ethyl and butyl branches at the ppm concentration level in polyethylene [4] or do a configurational characterization of various polypropylenes with different stereospecificity [5]. One of the major problems in pyrolysis-gas chromatography is the interlaboratory reproducibility, but the development of pyrolyzer units with uniform final pyrolysis temperature and reproducible rate of temperature rise has made it possible to achieve good quantitative results. However, temperature and heating rate calibrations of different probe analyzers are important for comparison purposes. Thus, specific analytical procedures have been developed to improve the reproducibility [6,7].

In this work, a pyrolysis - capillary gas chromatography method has been developed to characterize epoxy resin systems. This method, in conjunction with high performance liquid chromatography (HPLC), Fourier transform infrared spectroscopy (FTIR), and differential scanning calorimetry (DSC), is proposed as a means of controlling the quality of prepregs [8]. A prepreg consists of a reinforcing material such as woven graphite or fiberglass cloth impregnated with an organic matrix such as epoxy resin. These composites are widely used in the aerospace industry because they provide light weight, high tensile strength, and good resistance to fatigue. As such materials are being used in ever more critical applications, it has become necessary to improve the analytical methods used to assure their quality and performance.

Unlike HPLC or FTIR, PGC does not require special preparation of the prepreg before analysis. Samples can be analyzed at all stages of the reaction between the hardener and the epoxy resin. With HPLC or FTIR, it is necessary to perform an organic solvent extraction of the resin from the prepreg, and this becomes impossible beyond a certain degree of cure. Some qualitative work has been reported concerning the use of pyrolysis-gas chromatography to analyze epoxy resins [9-11]. In these analyses, a profile (chemical fingerprint) serves to distinguish different types of resin or to study their volatile content

[10,11]. The few reports of quantitative work in the literature are related mainly to the determination of the content of some monomers in different epoxy resin systems [9,12].

A pyrolysis-gas chromatography method has been developed to quantify the amount of hardener in an epoxy resin system and to characterize the extent of curing. The method has also been used to evaluate the aging of the prepreg during storage at room temperature. Moreover, PGC has been coupled with FTIR to identify some of the peaks in the chromatogram.

1.2 EXPERIMENTAL SECTION

1.2.1 Pyrolysis - Capillary Gas Chromatography

Pyrolyzers can be classified in two major groups: 1) pulse-mode pyrolyzers and 2) continuous-mode pyrolyzers. In our experiments, a pulse-mode pyrolyzer was used. A self-sensing, resistively heated electrical filament pyrolyzer from Chemical Data Systems with a pyrolysis unit Model 170 was coupled to a Model 6000 Varian gas chromatograph. The heating element is contained within a chamber through which the carrier gas flows and carries the pyrolysis products to the chromatographic column.

For the prepreg analysis, the sample was put in the centre of an open quartz tube about 20 mm long which was inserted in a platinum coil probe. The prepreg being sticky due to the epoxy resin, the sample location in the quartz tube was always reproducible and quartz wool was not necessary to hold it in the center of the tube. The probe was placed in the pyrolyzer interface installed at the head of the chromatographic column. The temperature of the interface was maintained at 200°C and helium was passed at 150 mL/min in order to prevent condensation of pyrolysis products inside the interface. The pyrolysis was done at 650°C for 10 seconds. At the maximum heating rate, the temperature rise is non-linear but reproducible. The coil element, holding the quartz tube, heats to 600°C in 600 milliseconds.

The capillary column was a 30 m x 0.259 mm fused silica column DB-17 from J&W Scientific Inc. It contains a chemically crosslinked and surface-bonded phase. This stationary phase, consisting of 50% methyl - 50% phenylsilicone, was slightly polar and the film thickness was 0.25 µm. The temperature of the injector was maintained at 250°C and the flame ionization detector was kept at 200°C. A constant split-ratio of 100:1 gave a flow rate in the column of about 1.5 mL/min. The column temperature program for analyses of epoxy resins and prepregs was the following: 50°C to 60°C (2°C/min) and

60°C to 250°C (10°C/min). Chromatograms were recorded on diskettes through the Varian data station Vista 401.

1.2.2 Pyrolysis - Gas Chromatography - Fourier Transform Infrared Spectroscopy

Fourier transform infrared spectroscopy was used to identify some of the peaks in the chromatogram. The gas chromatograph was coupled to a Nicolet 170SX FTIR through a Nicolet GC interface having a 3 mm i.d. x 42 cm gold-coated light pipe. The make-up gas was helium and the flow rate was adjusted to 50 mL/min. A narrow-range liquid-nitrogen-cooled mercury cadmium telluride (MCT) detector (5000-700 cm^{-1}) was used. A dry nitrogen purge was used for both optics and light pipe benches. Interferograms of 2048 data points were taken, resulting in spectra of 8 cm^{-1} resolution. Each acquired spectrum was an accumulation of sixteen scans requiring a total of 2.4 seconds.

Final identification of pyrolysis products was done with a Perkin-Elmer OV-101 capillary column measuring 60 m x 0.40 mm i.d. with a bonded stationary phase coating 5 µm thick. The thicker coating allows injection of a higher quantity of sample without loss of resolution. Columns with a 5 µm OV-17 type coating were not available.

1.2.3 Chemicals and Sample Preparation

The Rigidite 5208/WC3000 and Narmco 3203/WC3000 prepregs are manufactured by Narmco Materials Inc. They consist of woven graphite cloth (WC3000) impregnated with an epoxy resin system (about 42% by weight). The prepregs Ferropreg CE-9000-2/281 and CE-306/281 were made by the Composites Division of Ferro Corporation and are based on woven Kevlar cloth (type 281) with about 50% resin by weight. In all cases, the resin systems contain both epoxy and curing agent. Curing is very slow at room temperature and is normally accomplished by heating at 121°C (Narmco 3203 and Ferropreg CE-306) or 177°C (Rigidite 5208 and Ferropreg CE-9000-2). Epoxy resins Araldite MY 720 and Araldite 6010, and Hardener HT 976 were obtained from Ciba-Geigy Corporation. All other reagents were analytical grade.

In order to establish a calibration curve to determine the amount of hardener in an epoxy system, different mixtures of Hardener HT 976 and Araldite MY 720 epoxy resin were prepared in acetone solution (about 0.6 g in 25 mL). After evaporation of the acetone on a rotary evaporator, the mixtures were put under vacuum for one hour to remove the last

traces of solvent. The resulting viscous liquid was applied to the platinum ribbon probe with a spatula and pyrolyzed using the same conditions as for the coil probe.

1.3 RESULTS AND DISCUSSION

1.3.1 Optimization of Pyrolysis Conditions

The pyrolysis temperature and the sample mass inserted in the coil probe have been optimized for epoxy-graphite prepregs so as to achieve a good heat transfer to the resin. Reproducibility of the thermal treatment is obtained by controlling the temperature rise time and the holding temperature [13].

The effect of varying the pyrolysis temperature was studied with the Rigidite 5208 epoxy resin system. Briefly, this resin consists of three main components [14]. The major epoxy (67% by weight) is a complex mixture of about 60% tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) monomer and 40% higher oligomers and by-products. The second component (about 10% by weight) is the minor epoxy, a bisphenol A Novolac epoxy. Finally, the third component is 4,4'-diaminodiphenylsulphone (DDS) acting as a hardener (23% by weight).

Pyrolysis was done at different temperatures using about 0.5 mg of the neat Rigidite 5208 epoxy resin inserted in the coil probe. All other experimental conditions are as described previously. After the recording of the chromatogram, a second pyrolysis was dore at 1000°C on the residue from the same sample. It was found that the Rigidite 5208 was completely pyrolyzed at 1000°C. Thus, the percentage of residue at the lower pyrolysis temperature was estimated using the following formula:

$$\% \text{ Residue} = \frac{(\text{Area at } 1000°\text{C})}{(\text{Area at } 1000°\text{C}) + (\text{Area at pyrolysis temperature})} \times 100$$

where "area" corresponds to the total chromatogram area. In addition to the percentage of residue, we have calculated the relative area of the peaks eluting before 4 minutes with respect to the total area of the chromatogram. These peaks correspond to compounds of low molecular weight. Figure 1 illustrates the variation of these parameters as a function of the pyrolysis temperature. For a typical chromatogram, see Figure 5a.

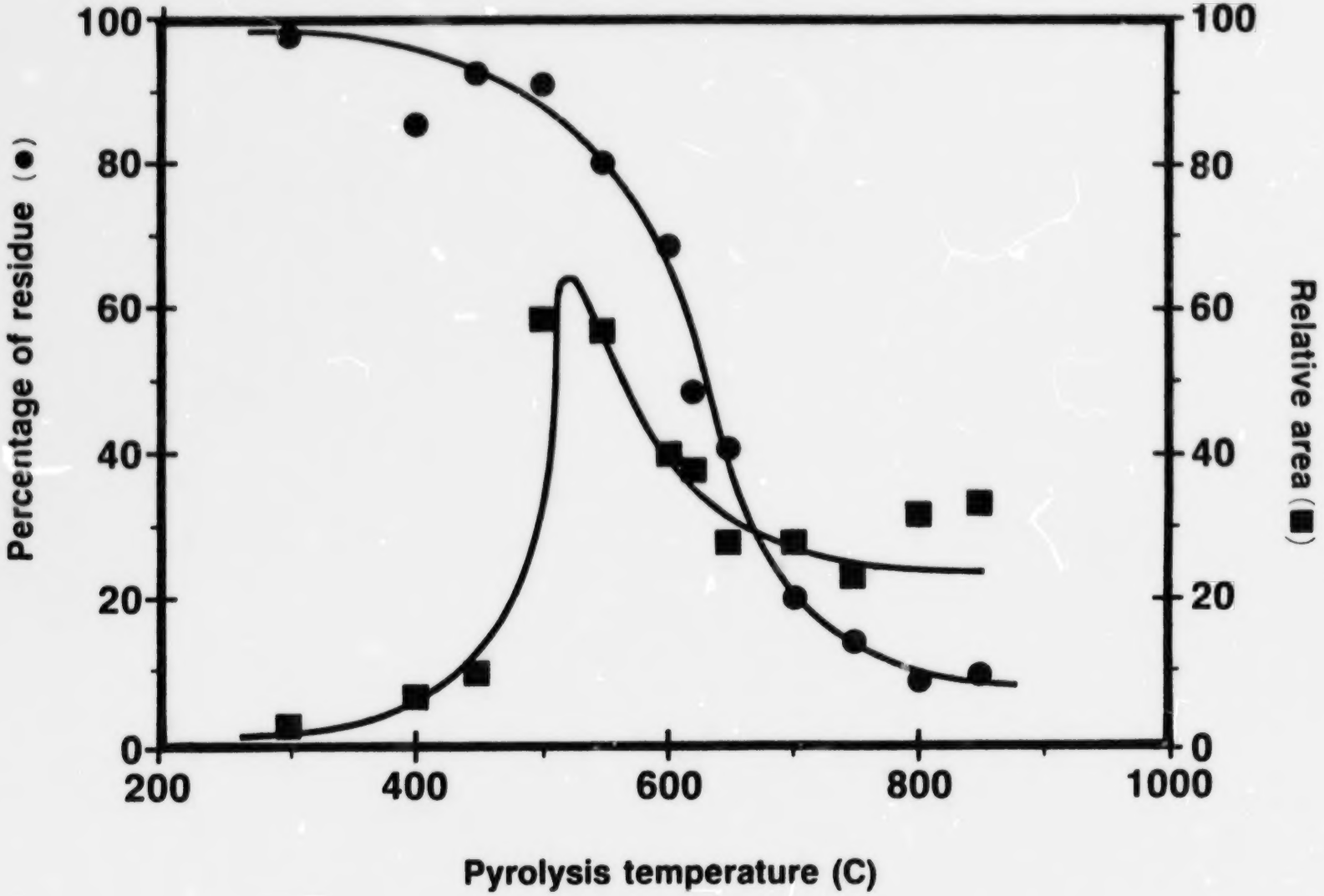


Figure 1. Dependence on the pyrolysis temperature of the percentage of residue and the relative area of the peaks eluting before 4 minutes for Rigidite 5208 epoxy resin.

At 700°C, the residue amounts to only 20% and the amount decreases slowly beyond this point, indicating that it is of no interest to increase the pyrolysis temperature. At this temperature, there is a lot of information as indicated by the large number of peaks observed in the chromatogram. However, if the peaks become too numerous, they are poorly resolved and it becomes difficult to make accurate quantitative measurements. At 700°C and over, the increase in the number of peaks may be due to an increase of secondary reactions corresponding to further degradation of the initial pyrolysis products, or it may be due to an increase of primary decomposition of the resin at higher temperatures. Below 600°C, the number and intensity of peaks are too small to permit a good quantitative analysis.

A maximum at about 525°C is observed on the plot of the sum of the relative areas for the peaks eluting before 4 minutes. As in the previous case, the decrease after 550°C may be due to an increase of secondary reactions involving these species, or it may be due to a change in the mechanism of the primary decomposition reaction. In any case, between 625°C and 800°C, this quantity remains approximately constant. Considering these two curves, a pyrolysis pulse of 650°C for 10 seconds gives a sufficient quantity of pyrolyzed resin to properly characterize the sample while at the same time avoiding an overly complex chromatogram.

The effect of the sample mass in the coil probe on the peak area has also been studied. Firstly, this effect was examined with 4,4'-diaminodiphenylsulphone (DDS) because it gives only one main peak after pyrolysis. A typical pyrogram is given in Figure 2. Experiments were done with sample masses varying between 0.5 and 2.5 mg. For this mass range, the variation of the area of the main peak as a function of the sample mass is linear with a squared correlation coefficient of 99.8%. However, there is sometimes a splitting of the main peak in the case of larger masses. For the calculation of the slope, the peak area for such cases corresponds to the sum of the two peaks. The peak splitting is probably caused by poor heat transfer to the sample, resulting in a two-step pyrolysis. It is recommended to use a sample mass of less than 1 mg to avoid such problems.

Secondly, the same variation was studied with Rigidite 5208/WC3000 prepreg to evaluate the effect of the graphite cloth on the pyrolysis of the epoxy resin. Six samples of this prepreg with different masses were pyrolyzed at 650°C for 10 seconds. Four well-separated peaks on the chromatogram were selected to verify the effect of the sample mass on the peak areas, and the results are shown in Figure 3. A linear relation is observed between 0.5 and 2.0 mg but deviations occur below 0.5 mg. Unlike a sample of a single material, a graphite-epoxy composite is heterogeneous and its pyrolytic behaviour at very low masses is different. In order to understand this behaviour, prepreg samples of

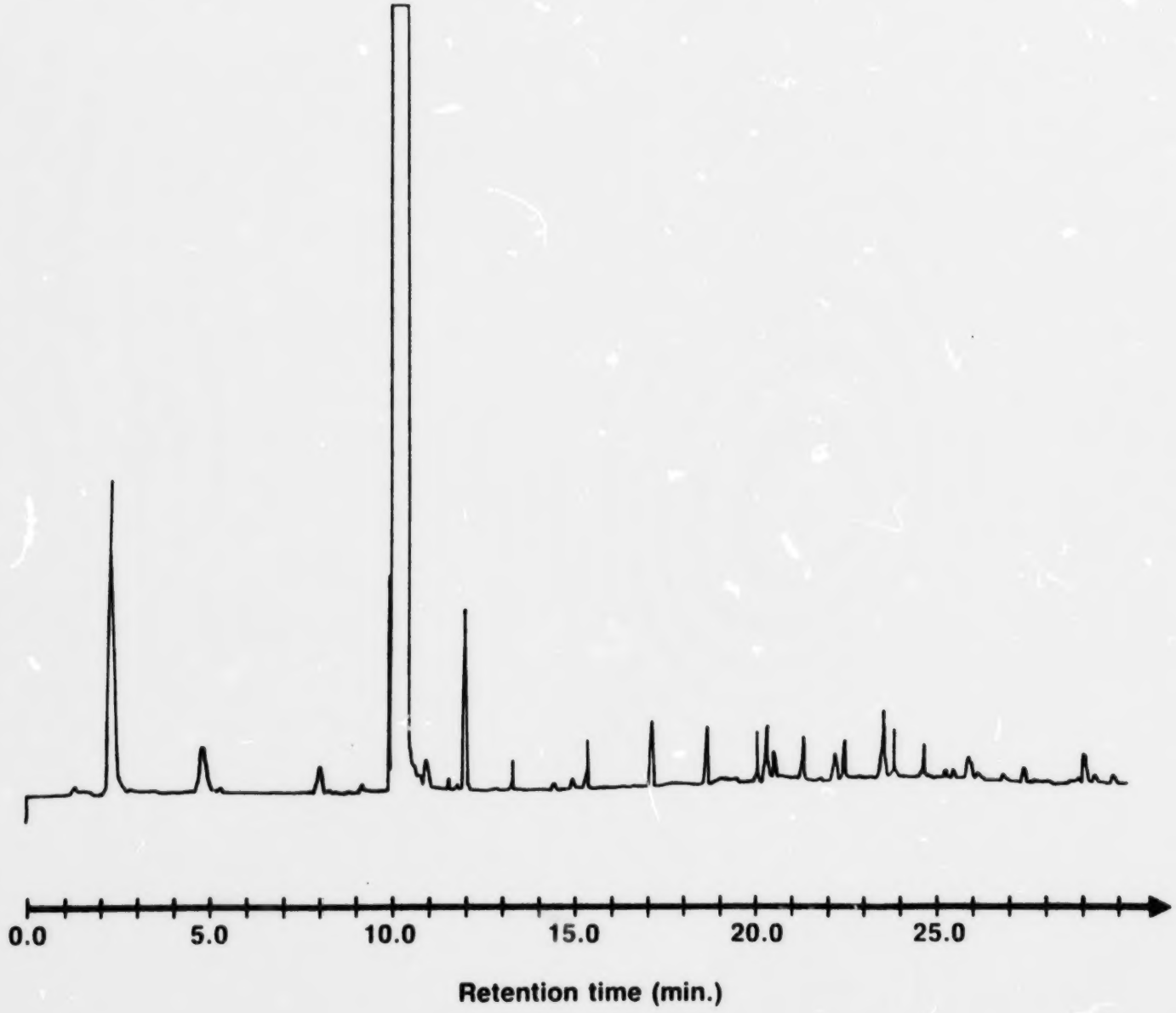


Figure 2. Pyrogram of 4,4'-diaminodiphenylsulphone (DDS).

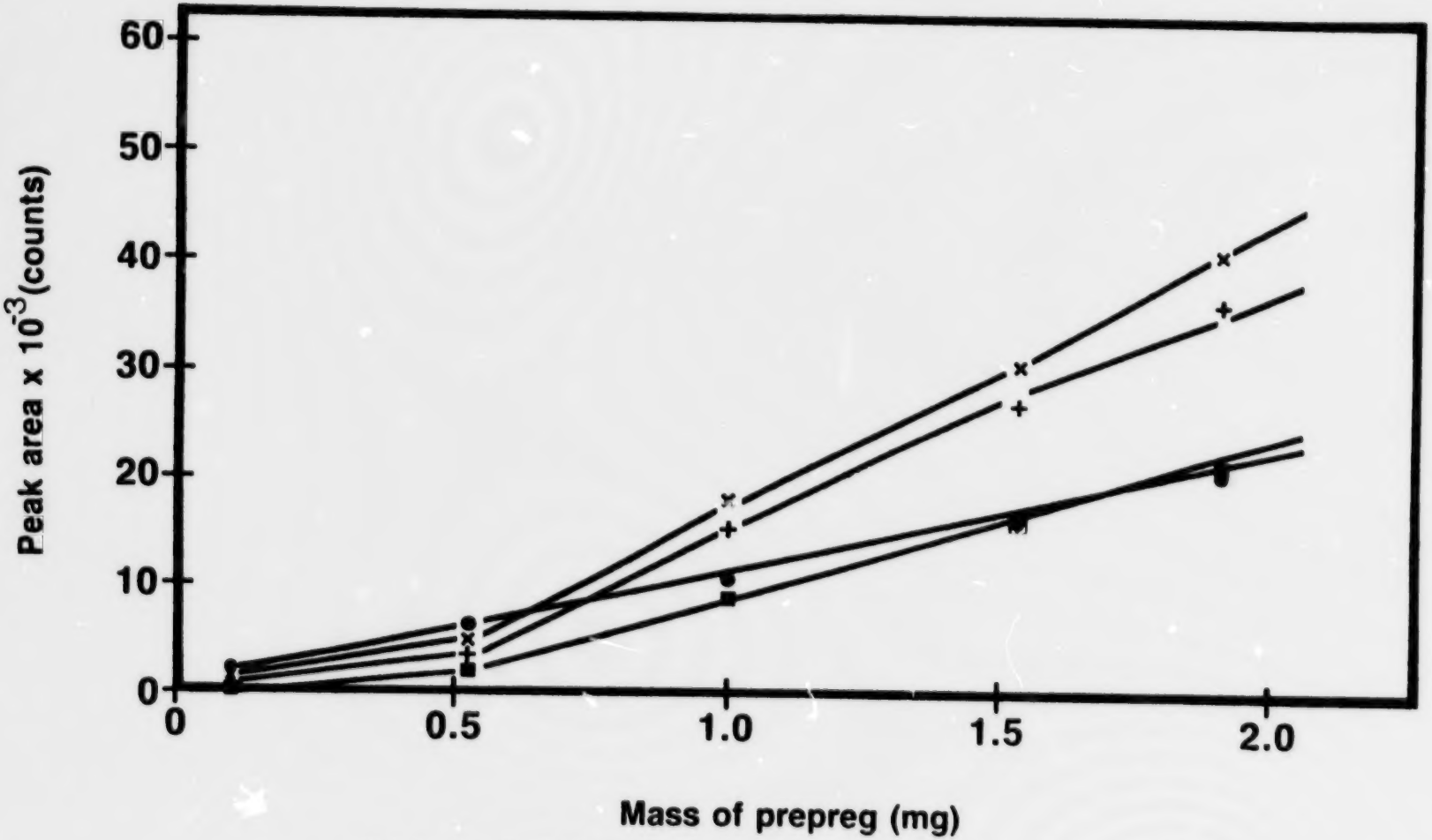


Figure 3: Variation of the peak area as a function of the sample mass for the Rigidite 5208/WC3000 prepreg.
(X) Peak 1, (+) peak 2, (■) peak 8, (●) peak 9
See Fig. 5A for peak identification.

different masses were pyrolyzed at 650°C for 10 seconds and the percentage of weight loss was calculated. Results are given in Table 1.

Table 1. Variation of the weight loss on pyrolysis as a function of the sample mass for Rigidite 5208/WC3000 prepreg.

Mass of prepreg (mg)	Weight loss (%) on pyrolysis
0.137	6.6
0.291	8.6
0.338	16.9
0.442	26.0
0.478	19.5
0.569	17.6
0.656	18.0
0.757	26.3
0.834	24.6
1.120	21.7
1.431	22.9

In spite of some scattering, the weight loss on pyrolysis is seen to be significantly lower for prepreg samples of less than 0.3 mg. This is attributed to the difficulty of preparing a representative sample of such a small size; it appears that such small samples contain a low amount of resin compared to the prepreg as a whole and thus the peak area and the percentage of pyrolyzed material are lower than at higher masses. In conclusion, it is recommended to work with a sample mass between 0.5 and 1.0 mg; this allows good heat transfer to the resin and good reproducibility in the analysis of prepregs.

1.3.2 Pyrolysis of Prepregs

Figures 4 and 5 show chromatograms of pyrolysis products of different epoxy resins and prepregs. Figures 4a and 5a correspond respectively to the Narmco 3203/WC3000 and Rigidite 5208/WC3000 prepregs. The 3203 resin system consists mainly of diglycidyl ether of bisphenol A (DGEBA) and dicyandiamide acting as a hardener. Figures 4b and 5b illustrate chromatograms of pyrolysis products of Ferropregs CE-306 and CE-9000-2. The woven Kevlar and graphite fabrics without epoxy resin were

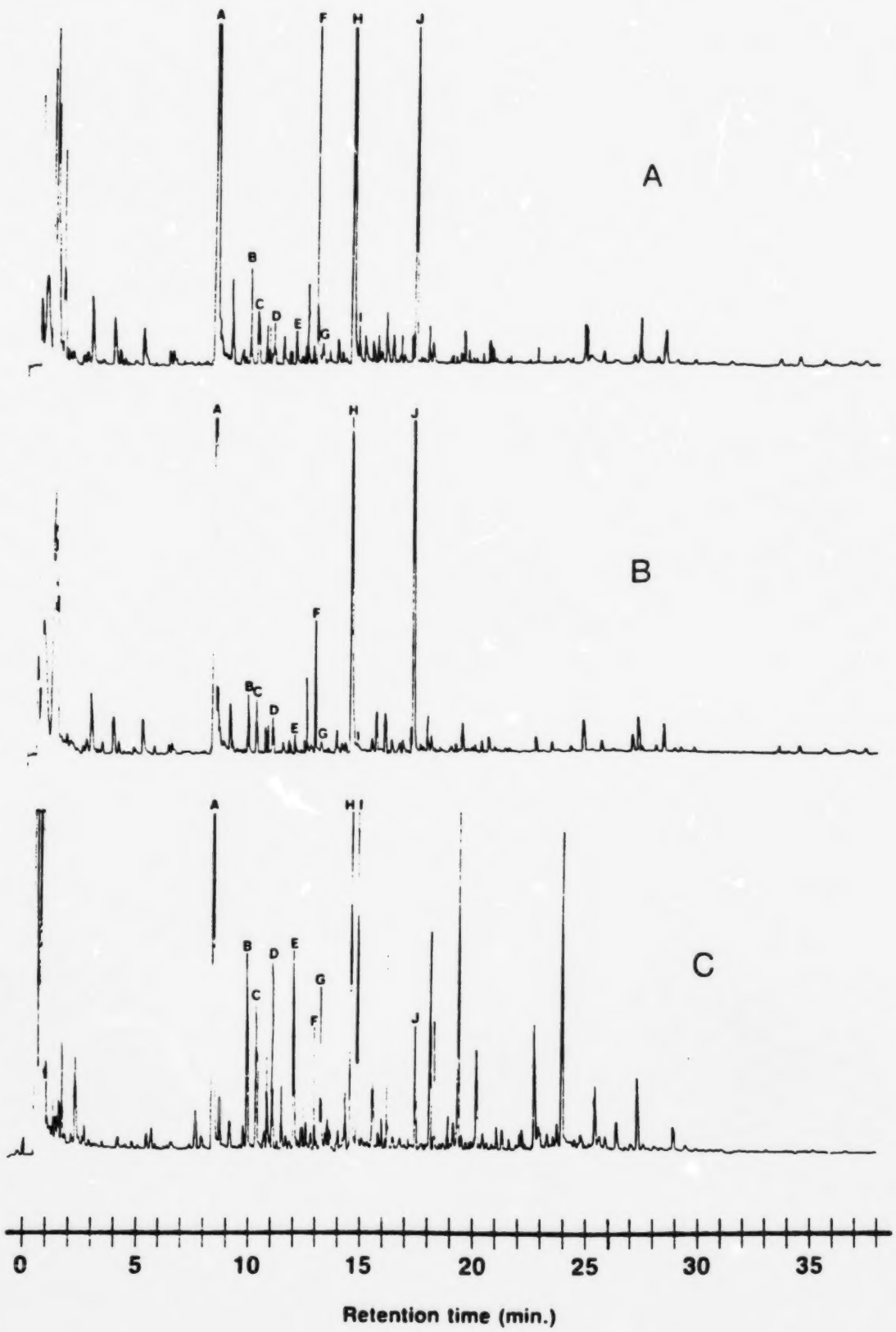


Figure 4. Pyrograms of Narmco 3203/WC3000 prepreg (A), Ferropreg CE306/281 prepreg (B), and Araldite 6010 epoxy resin (C).

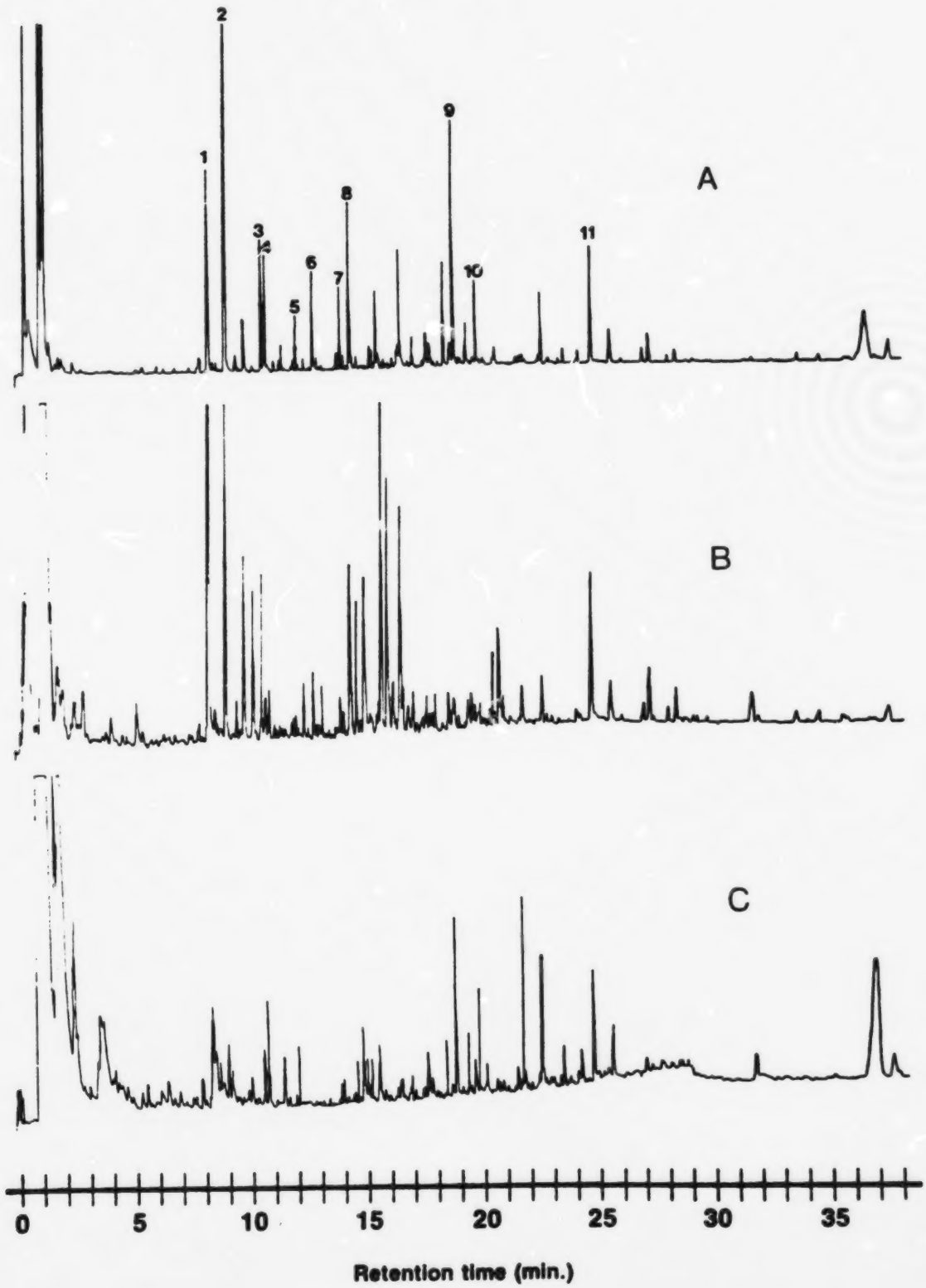


Figure 5. Pyrograms of Rigidite 5208/WC3000 prepreg (A), Ferropreg CE-9000-2/281 prepreg (B), and Araldite MY 720 epoxy resin (C).

pyrolyzed using the same conditions as for the prepregs and no significant decomposition products were observed. The chemical fingerprints of the four prepreg samples are sufficiently detailed to characterize their epoxy resin systems even if their composition is unknown. Comparison of the pyrograms of the Narmco 3203/WC3000 (Figure 4a) and Ferropreg CE-306 (Figure 4b) prepregs shows that a similar epoxy resin system has been used to make these composites. A visual correlation with the pyrogram of the neat epoxy resin Araldite 6010 (DGEBA), as shown in Figure 4c, illustrates that this type of resin is probably present in both. Also, the main peak arising from the pyrolysis of the hardener dicyandiamide has been found in the pyrolysis of these two prepregs at a retention time of about 8.1 minutes.

Examination of pyrograms of the prepregs Rigidite 5208/WC3000 (Figure 5a) and Ferropreg CE-9000-2 (Figure 5b) shows some similarities. The aniline peak (peak #2) is present in both chromatograms indicating the use of a similar aromatic hardener. Almost all the peaks of the pyrolysis products of Araldite MY 720, as illustrated in Figure 5c, can be found in the pyrogram of the Rigidite 5208 epoxy prepreg, thus confirming the presence of a TGDDM epoxy resin in this prepreg. However, although it is possible to find some matching peaks in the pyrograms of the Araldite MY 720 resin and the Ferropreg CE-9000-2, there are other important peaks in the chromatogram of this prepreg which do not appear in the chromatogram of the MY 720, suggesting that the prepreg contains another type of epoxy. This observation was confirmed by Fourier transform infrared spectroscopy. The resin systems of both prepregs were extracted with acetone, the extract was put on a KBr disk, and the solvent was evaporated. Spectra were recorded and the contribution of the DDS hardener was subtracted to obtain the IR spectrum of the epoxy resin. For the Rigidite 5208/WC3000 prepreg, FTIR confirms that TGDDM is the main epoxy resin, whereas the main resin in the Ferropreg CE-9000-2 appears to be of the "phenol Novolac" type.

1.3.3 Pyrolysis - Gas Chromatography - Fourier Transform Infrared Spectroscopy

The identification of the peaks generated by pyrolysis was attempted using a Fourier transform infrared spectrophotometer. Few data have been reported on the coupling of PGC with FTIR. We describe firstly the optimization of some instrumental parameters and secondly, a comparison of capillary columns with different film thicknesses.

1.3.3.1 Optimization of the make-up gas

The coupling of the gas chromatograph with the infrared spectrometer was optimized with a standard mixture of three esters: ethyl acetate, ethyl propionate and ethyl butyrate. The capillary column was inserted up to the bottom of the cell window of the FTIR light pipe through a heated transfer line. The temperature of the column and of the transfer line was 60°C and the temperature of the FTIR cell was maintained at 70°C.

The adjustment of the make-up gas is important to preserve the chromatographic resolution [15]. If the flow rate of the make-up gas is too low, the resolution is lost, as two peaks may be present in the light pipe at the same time. If the flow rate is too high, there is an increase of the limit of detection, because the concentration of sample in the light pipe at a given time is unnecessarily low. The ideal flow rate is one for which the time of residence in the light pipe is approximately the same as the chromatographic peak width. The flow rate of the chromatographic column was 1.5 mL/min. Using the Gram-Schmidt reconstruction based on the IR absorption in the light pipe, the peak intensity and peak width at half-height were measured for each peak at different flow rates of the make-up gas varying between 10 and 90 mL/min. This variation is shown in Figure 6 for ethyl acetate. Resolution increases up to a flow rate of 50 mL/min and then remains constant. There is no gain in resolution in working at higher flow rates. However, at flow rates greater than 60 mL/min, there is a decrease in the intensity of the peak. Thus, a flow rate for the make-up gas of about 50 mL/min is recommended for the present system to achieve the best compromise between resolution and detection.

1.3.3.2 Pyrolysis with a capillary column coated with a film of thickness 0.25 μm

The pyrolyzer interface was put on the head of the chromatographic column coupled to the FTIR in order to identify the pyrolysis products. The first experiment was the pyrolysis of DDS because this product generates few peaks. For this experiment, the temperature of the transfer line was 260°C and the temperature of the light pipe was 270°C. The Gram-Schmidt reconstruction is given in Figure 7. It consists of two peaks which correspond to the two main peaks of the chromatogram obtained with the FID detector (Figure 2). A search of the EPA Vapor Phase library for the second peak identified it as aniline. The first peak was identified as SO_2 by a manual search. Thus, for the hardener, the pyrolysis fragmentation pattern is:

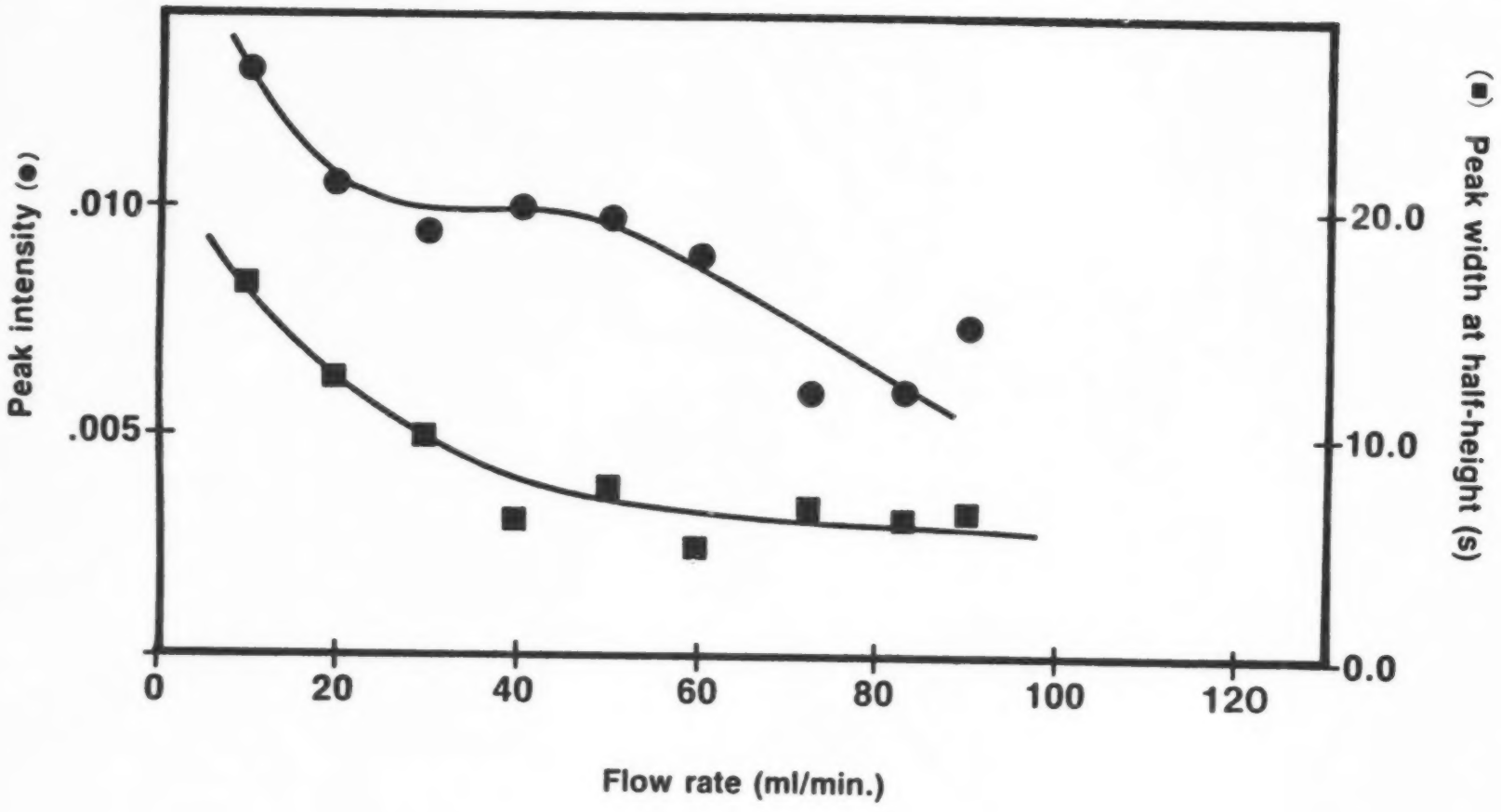


Figure 6. Variation of the peak intensity and the peak width at half-height as a function of the flow rate of the make-up gas for ethyl acetate.

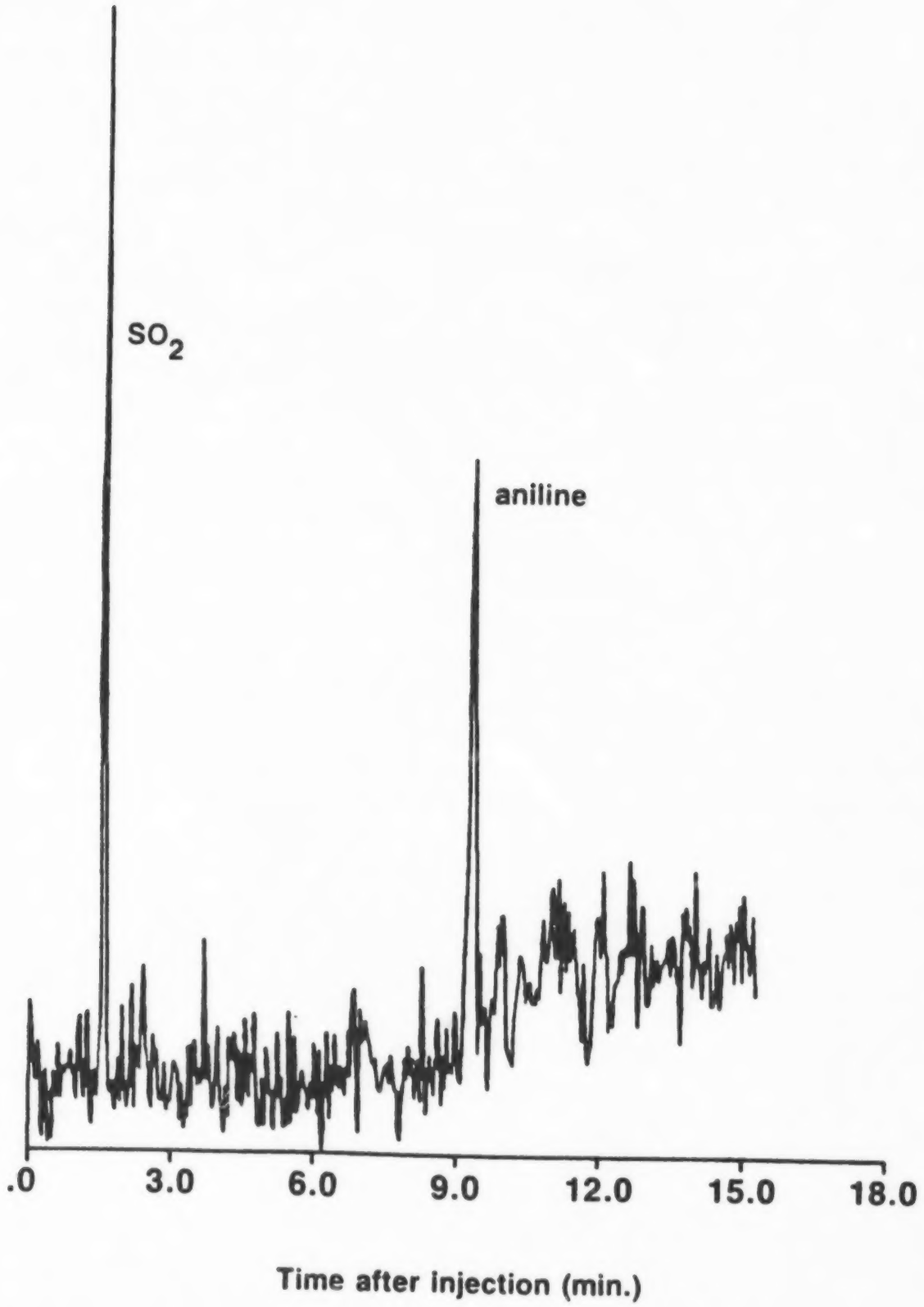
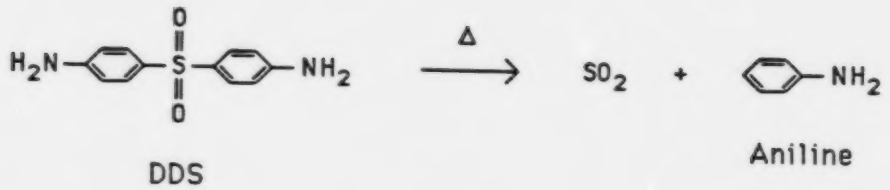


Figure 7. Gram-Schmidt reconstruction for the pyrolysis - capillary gas chromatography of DDS. Column: DB-17, 30 m x 0.259 mm i.d., film thickness 0.25 μm.



Other small peaks observed in the FID chromatogram were not detected by the infrared detector because the quantity is too small. A typical pyrolysis involves a sample mass of about 0.5 mg and, with a split ratio of 100:1 at the injector, the quantity of product injected on the column is about 5 µg. As the small peaks correspond to less than 1% of this amount, it is impossible to detect them with infrared detection because the limit of detection is about 50-100 ng.

A similar experiment was performed using Rigidite 5208 resin. In this case there are many more pyrolysis products and the quantities involved are smaller, so they were not detected by FTIR. It is impossible to inject a larger quantity on the chromatographic column without damaging it. One solution is to use a column with a film thickness of 1 or 5 µm. These columns permit the injection of a larger quantity of sample without a loss of resolution [16].

1.3.3.3 Pyrolysis with a capillary column coated with a film of thickness 5 µm

An OV-101 capillary column with a film thickness of 5 µm was installed in the gas chromatograph and a pyrolysis of 35 mg of Rigidite 5208 epoxy resin was done. The Gram-Schmidt reconstruction for this pyrolysis is given in Figure 8. Twelve compounds have been identified by FTIR. It was not possible to detect all the peaks observed with the flame ionization detector because the limit of detection of the FTIR is still too high. Moreover, it is difficult to pyrolyze efficiently more than 20 mg of sample with the probe used.

Unfortunately, the separation with the DB-17 column (Figure 5a) is bad at the beginning of the chromatogram. Thus, the correlation of the peak retention between the two columns is very difficult. However, on the DB-17 column (Figure 5), we have found that phenol is the peak #1 and aniline is the peak #2. These correspond to peaks #9 and

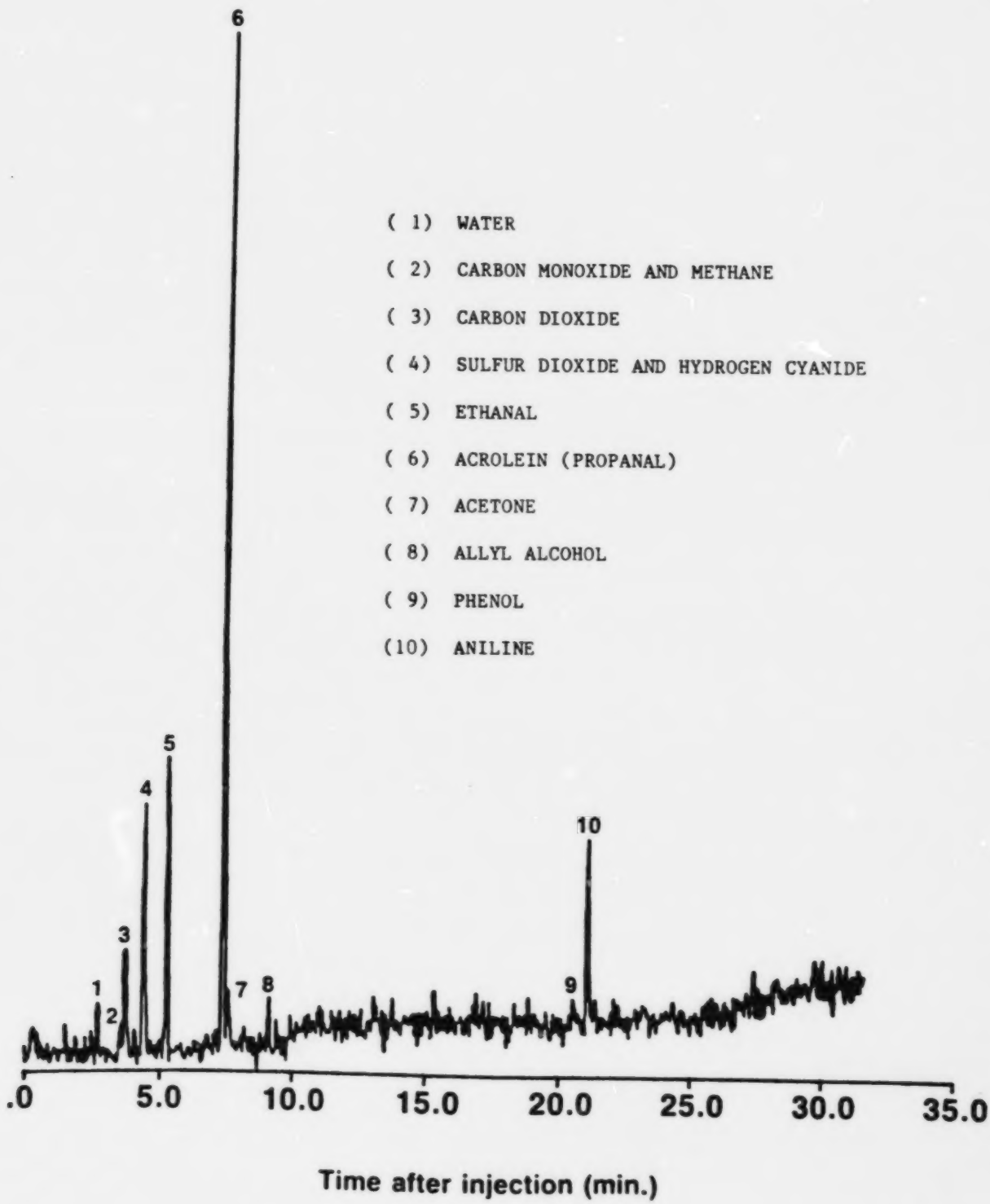


Figure 8. Gram-Schmidt reconstruction for the PGC of Rigidite 5208 epoxy resin. Column: OV-101, 60 m x 0.40 mm i.d., film thickness 5 μm.

#10 in Figure 8. All other compounds identified on the OV-101 are grouped before 3 minutes on the DB-17 column and are not well separated. Moreover, we have no indication as to the peak identities after the peak of aniline.

In conclusion, the capillary column with a film thickness of 5 μm allows the injection of a larger amount of sample but it is not enough to analyze adequately all peaks. However, the identification is sufficient to characterize quantitatively an epoxy resin.

1.3.4 Quantitative Determination of the Hardener in the Epoxy Resin System

Mixtures of the Hardener HT 976 (DDS) with Araldite MY 720 epoxy resin were prepared and analyzed by PGC. The ratio, R, of the aniline peak area (peak #2) against the phenol peak area (peak #1) has been used to determine the percentage of DDS in the mixture. If this percentage is x, then for x grams of DDS, (100-x) grams of epoxy are present in the system. Thus, if the quantities of DDS and epoxy are respectively associated with the aniline and phenol peaks, the ratio P, where P equals x/(100-x), should be linearly related to the ratio R. Results are shown in Table 2.

Table 2. Variation of the ratio of the aniline peak against the phenol peak as a function of the amount of DDS for different mixtures of DDS and TGDDM

Percentage of DDS (by weight)	Ratio P DDS/epoxy	Ratio R aniline peak/phenol peak
10.25	0.144	0.108
14.91	0.175	0.149
20.14	0.252	0.175
25.36	0.340	0.257
30.49	0.439	0.317

The relation is linear and is described by the following equation:

$$P = (1.5 \pm 0.1) * R + (0.04 \pm 0.02)$$

with a squared correlation coefficient of 98.3%. This relation is valid only for the ribbon probe. The main advantage of using the ratio of two peaks in PGC is that the final result is independent of the sample mass pyrolyzed if this mass is less than 2 mg. On the other hand, the chemical composition of the sample must be known to be sure that no other compounds can generate phenol or aniline which will influence the ratio. Thus, PGC could be a good quality control method for a manufacturer to evaluate the content of hardener in an epoxy resin with no sample preparation when experimental conditions and the nature of the product are well established. PGC can also be used advantageously to control the batch-to-batch reproducibility of an epoxy resin system.

1.3.5 Curing of the Rigidite 5208/WC3000 Prepregs

A systematic study of the curing of the prepreg Rigidite 5208/WC3000 has been done using pyrolysis - gas chromatography. Samples were cured for 1 hour at different temperatures. The ratio of each peak in the chromatogram (Figure 5a) against the aniline peak (peak #2) was calculated in order to establish a correlation between the chromatogram and the degree of cure. Table 3 illustrates the results obtained for some peaks.

Table 3: Ratio of some peaks of the pyrogram of Rigidite 5208/WC3000 prepreg against the aniline peak as a function of the curing temperature for a one-hour cure.

Peak #	Ratio of the peak area against the aniline peak area						
	Uncured	75°C	100°C	120°C	140°C	160°C	180°C
3	12.1	14.2	14.6	12.6	13.0	20.7	25.5
4	11.5	11.5	12.0	12.8	12.5	16.3	19.9
5	5.0	5.8	6.4	5.3	5.3	8.4	9.4
6	11.3	10.8	11.6	12.2	13.5	10.9	10.7
10	5.2	6.0	7.2	8.6	6.8	4.4	2.7
11	9.6	14.3	11.7	8.4	6.5	6.5	2.2

A definite increase is observed for peaks #3, #4 and #5, indicating either a decrease in the amount of aniline or an increase of the compound of these peaks or both. Peak #4 is probably the best choice to follow the curing. It is also interesting to note that some peaks like peaks #10 and #11 show a maximum at a certain temperature indicating a different

decomposition behaviour in more highly cross-linked material. Thus, it is possible to follow the curing of a prepreg to an advanced stage with minimal sample preparation using pyrolysis - capillary gas chromatography.

1.4 CONCLUSIONS

(1) Pyrolysis of epoxy prepreg at 650°C for 10 seconds gives a sufficient quantity of pyrolyzed resin without producing too complex a mixture of pyrolysis products.

(2) A sample mass of prepreg varying between 0.5 mg and 1.0 mg is recommended to obtain good heat transfer to the resin and reproducible results.

(3) Coupling of pyrolysis - capillary gas chromatography with Fourier transform infrared spectroscopy permits rapid identification of pyrolysis products without further manipulation.

(4) In PGC - FTIR with a 42 cm x 3 mm light pipe, a flow rate for the make-up gas of 50 mL/min has been found to be optimum with respect to the resolution and the detection.

(5) The use of capillary columns with a film thickness of 5 μm facilitates the identification of pyrolysis products by permitting the pyrolysis of samples weighing 20 mg.

(6) The ratio of the aniline peak against the phenol peak has been related to the percentage of DDS in an epoxy resin system.

(7) Curing and aging of the prepreg can be followed by PGC but the method is not sensitive to small changes.

2. THERMAL ANALYSIS

2.1 INTRODUCTION

Various analytical techniques have been used to characterize fibre-reinforced organic-matrix composites. The development of analytical methods for characterization of epoxy-graphite composites using high-performance liquid chromatography or Fourier transform infrared spectroscopy has been reported previously [17-19]. These techniques allow the monitoring of small variations in the chemical composition of an epoxy resin formulation. In the first part of this report, a pyrolysis-gas chromatographic method has been developed and applied to an epoxy-graphite prepreg. This method involves a rapid heat transfer (~ 1000°C/s) to the sample in order to decompose the epoxy resin. Decomposition products are immediately injected and separated on a capillary gas chromatographic column. The chromatogram gives a unique chemical pattern of the epoxy resin which can be used to characterize the systems studied. Unfortunately, in PGC, the aging of an epoxy-graphite prepreg can be evaluated only if variations in the chemical composition of the resin are relatively large.

A variant of this pyrolysis method involves a slow transfer of heat to the sample (5 - 10 °C/min). This group of techniques, known collectively as thermal analysis, can give useful information on the composition, structure and physicochemical behavior of the epoxy-based prepreg. Different thermal analysis methods are available to characterize epoxy resins [20-21]. Among them, the most popular are differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and thermomechanical analysis (TMA). In this work, only DSC and TGA will be considered.

An accepted definition of thermal analysis as given by Mackenzie [22] and the International Confederation for Thermal Analysis (ICTA) is: "A group of techniques in which a physical property of a substance and/or its reaction products is measured as a function of temperature whilst the substance is subjected to a controlled temperature program." More specifically, in TGA, the mass of the sample is continuously monitored during heating whereas, in DSC, the quantity of heat released or absorbed by the sample is measured as a function of a controlled temperature program.

Thermal analysis methods will be applied to the Narmco Rigidite 5208 system, which has been described in detail elsewhere [17]. Briefly, the resin consists of three main components. The major epoxy (about 67% by weight) is a complex mixture of about 60% tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) and 40% oligomers and by-products. The second component (about 10% by weight) is the minor epoxy, a bisphenol

A Novolac epoxy. Finally, the third component is 4,4'diaminodiphenylsulphone (DDS) acting as a hardener (about 23% by weight).

There are some reports in the literature on the analysis of Narmco 5208 neat resin by DSC [23-25]. However, most of the work has been related to the determination of kinetic parameters of cure reactions involving the main epoxy (TGDDM) and the amine hardener (DDS). A review of this subject is given in Part 1 [17]. The main purpose of this work is to develop an accurate DSC method to characterize the Narmco 5208 prepreg and to compare this method to other analytical techniques in order to examine its advantages and disadvantages as a quality control method.

The application of heat to an epoxy resin system causes reactions between epoxy and hardener. The main goal of a DSC experiment is to evaluate the enthalpy corresponding to the curing reaction. However, with an epoxy-graphite prepreg, reproducibility in the determination of enthalpy is a major problem because the percentage of organic resin in the prepreg can vary significantly from sample to sample, even when they come from the same sheet of prepreg, due to nonuniform distribution of resin [25]. Organic solvent extractions of different samples taken from the same batch of prepreg likewise show a significant variation in the quantity of resin extracted [26]. In the case of Narmco 5208 prepreg, it varies from 40% to 45%. As the enthalpy is related to the epoxy resin only, it is important to find a method to accurately measure the content of resin in a sample after a DSC experiment. The mass of a typical sample used in a DSC experiment varies from 30 to 40 mg. Assuming a graphite fibre content of about 60% by weight, the quantity of epoxy resin varies from 12 to 16 mg. Thus, the method used to evaluate the mass of resin must be precise in order to obtain accurate and reproducible enthalpy values.

The decomposition of the resin without oxidation of the fibre reinforcement can sometimes be achieved in an inert atmosphere and the quantity of resin can be found using a simple thermogravimetric analysis [20,21,27,28]. However, in practical terms, thermal decomposition with an inert gas such as nitrogen can create some problems. With some epoxy resin systems, the decomposition can be incomplete, leading to false results. Also, the decomposition of the resin without oxygen does not generate small molecules such as CO_2, CO or H_2O. Volatiles formed during the decomposition condense on the different parts of the instrument and contaminate the system. Thus, the possibility of using a TGA method with either oxygen or nitrogen as atmosphere has been examined. This method in conjunction with a DSC experiment performed under appropriate experimental conditions will give accurate values of enthalpy for the curing reaction.

2.2 EXPERIMENTAL SECTION

2.2.1 Materials

The composite system studied was the Rigidite 5208/WC3000 system sold by Narmco Materials, Inc. The reinforcement consists of Celion graphite fibres, 3000 fibres per yarn, woven in an 8-harness satin pattern (each warp yarn passing alternately over seven fill yarns and under one fill yarn). The woven fabric is impregnated with Narmco 5208 resin to a nominal resin content of 42% by weight and the prepreg is supplied on a plastic backing sheet in rolls. The recommended cure schedule consists of a one-hour dwell at 135°C (275°F) followed by a two-hour cure at 177°C (350°F). The resin is commonly referred to as simply "Narmco 5208". The following samples of the Narmco 5208 system were supplied by Canadair Ltd.:

Prepreg, Batch Number 1010
Prepreg, Batch Number 1014
Prepreg, Batch Number 1101
Prepreg, Batch Number 1103
Prepreg, Batch Number 1104
Neat resin on plastic backing sheet, Batch Number 1047
Neat resin in bulk form, Batch Number 1023.

Prepreg and reactive resin samples were stored in a freezer at all times except for sampling and performance of experiments. Samples of the following components were obtained from the respective companies:

Ciba-Geigy Araldite MY 720 epoxy resin (TGDDM), Lot Y5085
Ciba-Geigy Hardener HT 976 (DDS), Lot IL 2096
Celanese Epi-Rez SU-8 (bisphenol A Novolac epoxy), Lot L11-82182.

These were stored in a refrigerator.

2.2.2 Thermogravimetric Analysis

The thermobalance used was a Model B70 from SETARAM, and is equipped with a graphite resistance furnace. Data are collected via a Hewlett-Packard system. The balance is precise to ±30 μg over a long period of time. The output signal of the balance in mV is transformed into mg using a sensitivity factor which is known to 0.3%. The loss of weight is thus measured within 0.3%.

Samples were analysed either in alumina or platinum crucibles. The heating rate was maintained constant at 10°C/min. For isothermal experiments, the temperature of the furnace was increased rapidly (25°C/min) to the selected temperature and maintained at this level.

2.2.3 Differential Scanning Calorimetry

The differential calorimeter was a SETARAM Model CDP111. It consists of an oven, an electronic temperature programmer, and a signal amplifier, and is interfaced with a Hewlett-Packard HP-85 microcomputer to store the raw data and to perform different mathematical treatments. The calorimeter is equipped with two heat flow sensors (Calvet type), one for the sample, the other for the reference, which are located in the centre of a thermostatted block. Each sensor consists of about 150 thermocouples almost completely surrounding a cylindrical sensitive zone (20 mm long, 7 mm in diameter). The calorimetric signal is the difference between the signals from the sample and the reference sensors.

Samples of prepreg (30-40 mg) were weighed in open platinum crucibles and suspended vertically in the calorimeter. An empty platinum crucible was used as reference. The electrical signal in μV was transformed into mW (heat flow) by a fourth degree equation obtained from prior calibration of the instrument. In scanning mode, the signal in mW was recorded as a function of the real temperature of the sample. Calculation of enthalpy was done by measuring the surface area under the DSC curve.

2.3 RESULTS AND DISCUSSION

2.3.1 Thermogravimetric Analysis

2.3.1.1 Nitrogen atmosphere

The easiest method to obtain the mass of resin in an epoxy-graphite prepreg is to pyrolyze the resin in an oven at constant temperature and to weigh the graphite fibres. Some epoxy systems undergo complete decomposition at certain temperatures under nitrogen [27,29]. Figure 9 shows the TG curve for Narmco 5208 neat epoxy resin (batch #1023) obtained with nitrogen. The weight loss is fairly constant at 66.1% between 750 and 900°C and the curve shows that it is impossible to completely decompose this epoxy system in a nitrogen atmosphere below 1200°C.

The other sample of Narmco 5208 neat epoxy resin (batch #1047) gives a weight loss of 66.9% using the same experimental conditions. As the percentage of decomposition appears relatively constant at 900°C, some experiments were done to evaluate the percentage of epoxy resin in a prepreg through an isothermal decomposition. Samples of neat resin were put in an oven maintained at 900°C with nitrogen as atmosphere. Unfortunately, when the samples are put in the oven, the resin overflows the crucible and the loss of resin is significant. It is necessary to control the rise of temperature and thus, a thermobalance is simpler to use.

A TG curve of the epoxy-graphite prepreg with nitrogen will give the mass of the decomposed epoxy resin. This mass is known to 0.5%. A correction using the value found for the decomposition of the neat epoxy resin (~ 66%) will lead to the mass of resin in the prepreg. The relative error of this correction is 1.5%. Thus, the final mass of epoxy resin will have a relative error of 2%. Typically, if the quantity of resin in the prepreg is about 20 mg, the absolute error on the mass is about 0.4 mg. This error is not negligible for the determination of accurate enthalpy values, and this method also requires that the composition of the epoxy resin be relatively constant in order to minimize the error involved in the correction.

Thus, in spite of the tendency of graphite to decompose in an oxidizing atmosphere, some TG curves were obtained for Narmco 5208 prepreg in an oxidizing environment in order to find a method which has a smaller relative error and is less sensitive to the chemical composition of the epoxy resin.

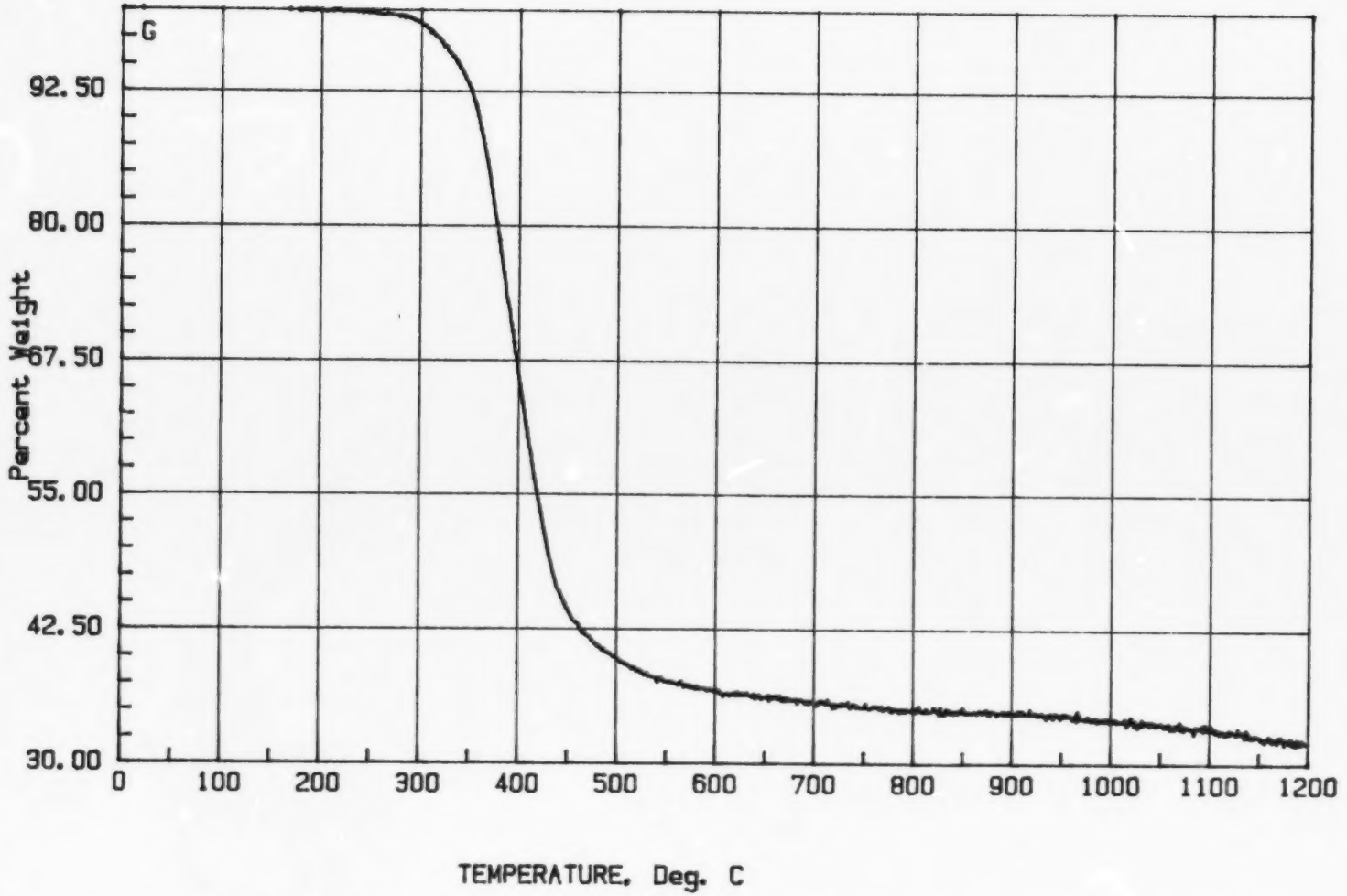


Figure 9. TG curve of Narmco 5208 neat epoxy resin. Gas: nitrogen; heating rate: 10°C/min; mass of resin: 22.4 mg.

2.3.1.2 Oxygen atmosphere

The purpose of the following experiments was to find an ideal temperature for achieving the isothermal decomposition of epoxy resin without oxidation of graphite fibres. Initial thermograms were obtained in dynamic mode at a heating rate of 10°C/min with oxygen as atmosphere in order to localize the different decomposition steps. Thermograms for the neat epoxy resin Narmco 5208 (batch #1023), for graphite fibres alone, and for an epoxy-graphite prepreg (batch #1103) are shown in Figures 10, 12, and 13 respectively.

The derivative TG curve for the neat 5208 resin (Figure 10) shows two distinct peaks indicating a two-step decomposition. Similar results have been reported in the literature for different epoxy resin systems [27, 30]. The first decomposition begins at about 260°C and corresponds mainly to the release of volatile products. This step is characterized by the presence of a strong odour. The second decomposition is odourless and begins at about 450°C. It is associated with the oxidation of the carbonized residue. At 610°C, the resin is completely oxidized in an oxygen atmosphere.

The change of slope in the TG curve at about 460°C has been used to calculate the percentage of resin. Two points have been selected as shown in Figure 11. Point 1 corresponds to the inflexion point at 460°C and point 2 is the extrapolation of two sections of the curve as shown in the figure. These correspond respectively to 51.8% and 47.6%. Assuming that these points of decomposition are invariant, they can possibly be used to determine the percentage of resin .

Figure 12 illustrates that the decomposition of graphite fibres in oxygen is a one-step process. There is a slow oxidation up to 550°C followed by a much faster oxidation. At 670°C, they are completely oxidized.

The TG curve of the Narmco 5208 prepreg (batch #1103) is given in Figure 13. The three decomposition steps observed in the previous figures are distinguishable. The first decomposition is detected until 450°C and the second decomposition, which corresponds to the oxidation of carbonized epoxy resin, is observed between 450 and 600°C. Finally, the decomposition of graphite fibres is recorded between 600 and 780°C. The oxidation of the graphite fibres is displaced toward higher temperature when the fibres are embedded in the epoxy resin, as compared to the result obtained with fibres alone. In a prepreg, the graphite fabric is completely covered with epoxy resin and it is reasonable to assume that the graphite fibres are not oxidized significantly until the resin coating has decomposed.

The epoxy resin without reinforcement is almost totally oxidized at about 600°C, the same temperature at which the graphite fibres begin to be oxidized. Thus, it may be

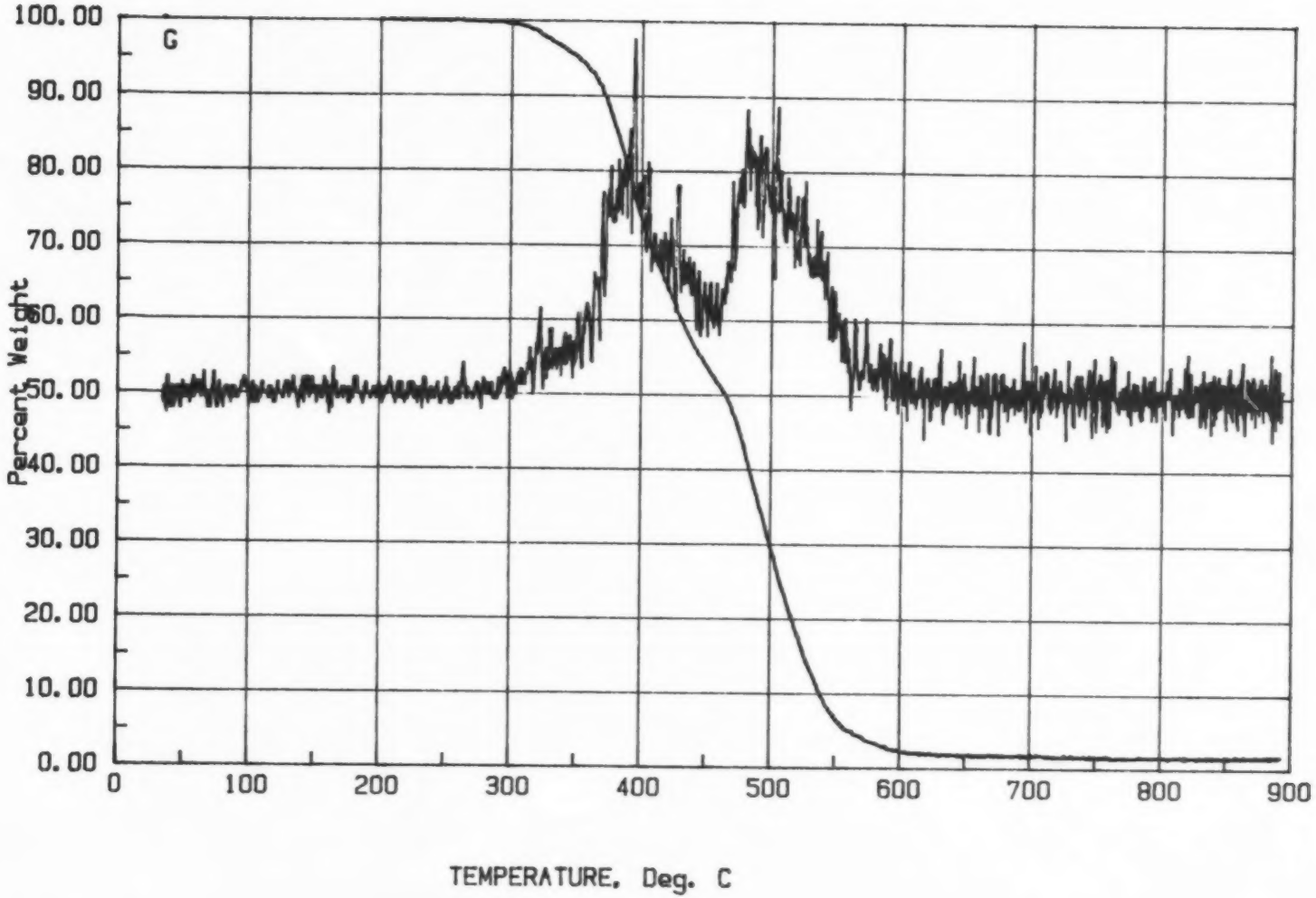


Figure 10. TG curve of Narmco 5208 neat epoxy resin. Gas: oxygen; heating rate: 10°C/min; mass of resin: 32.6 mg.

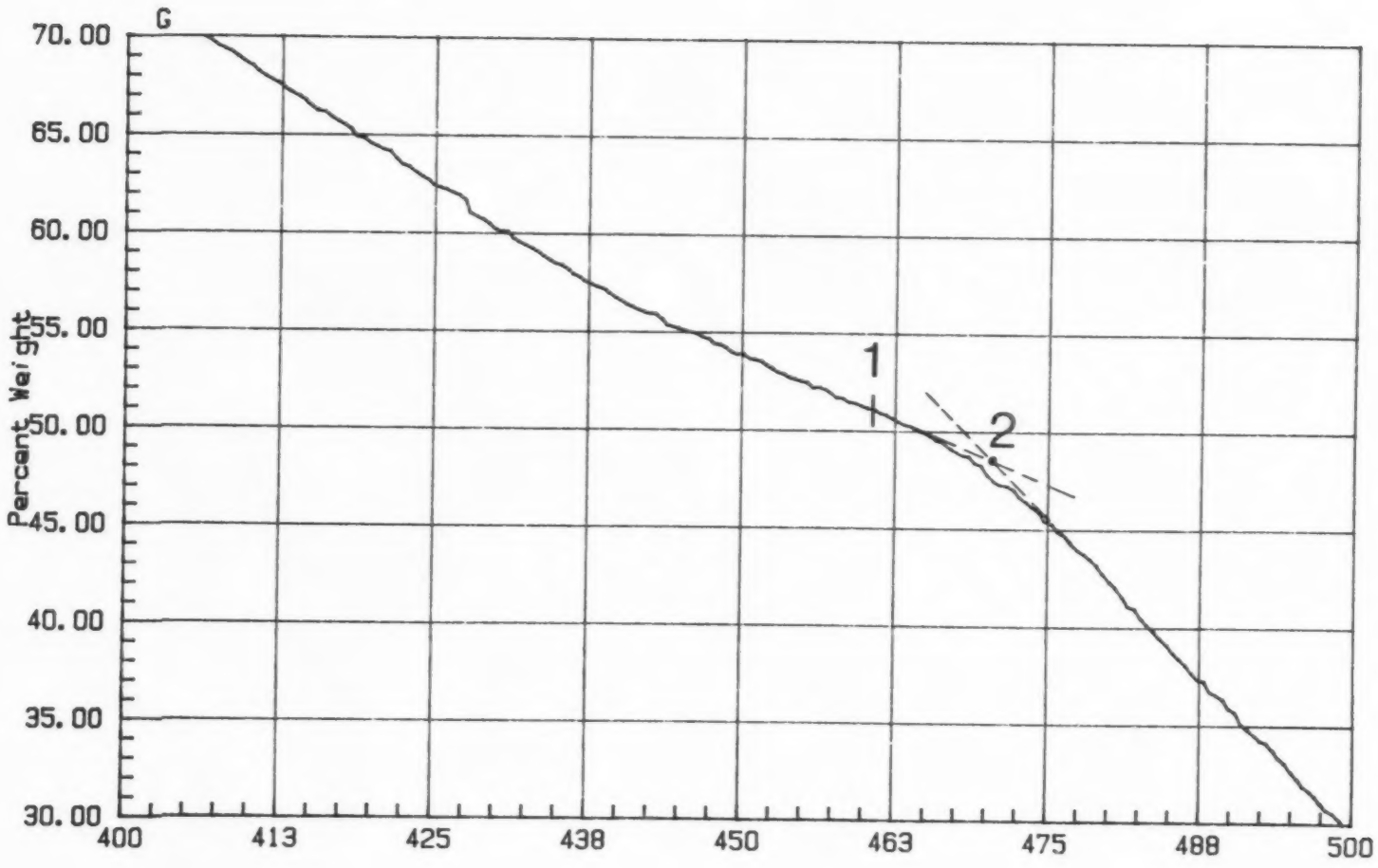


Figure 11. Enlarged area of Figure 10.

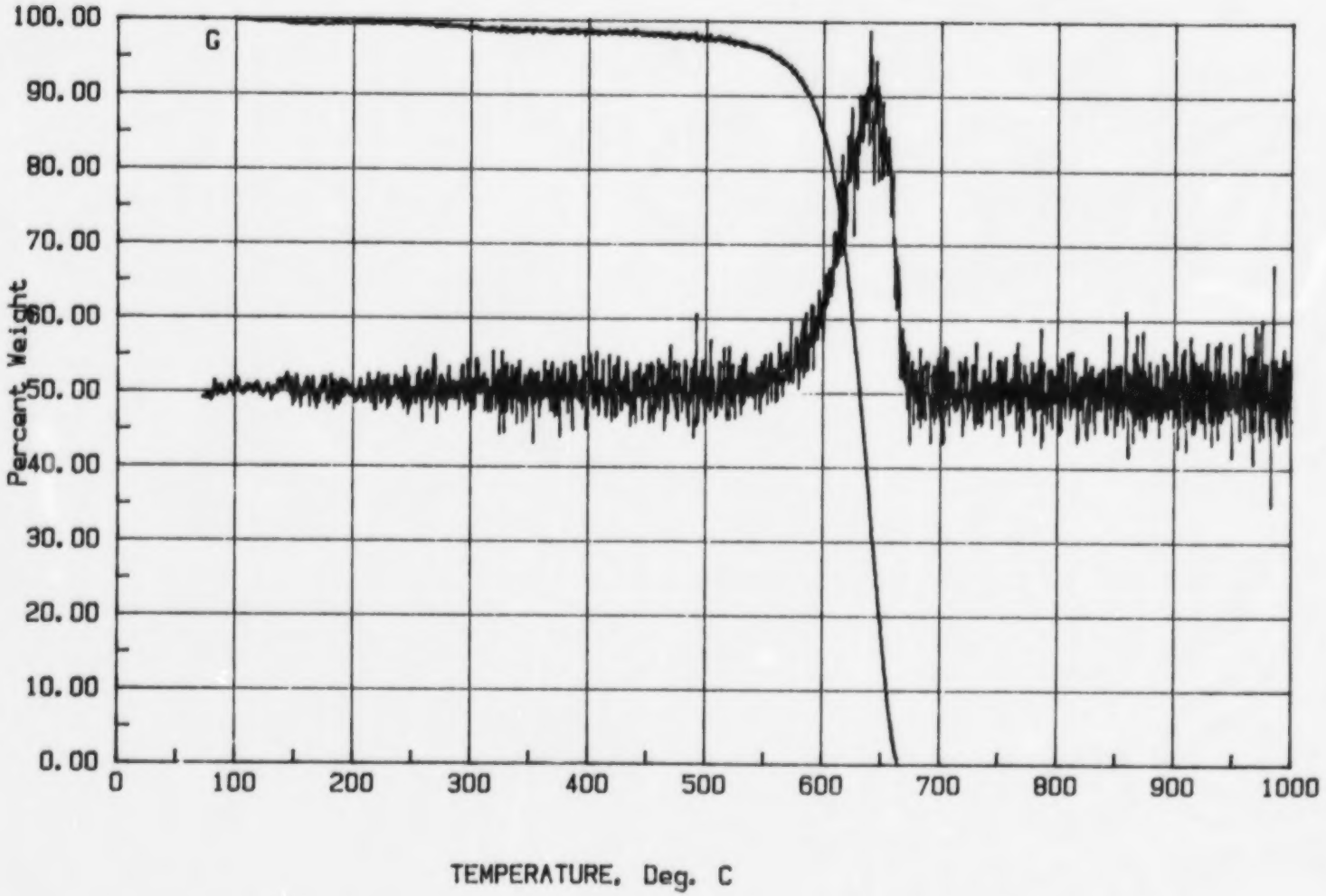


Figure 12. TG curve of graphite fibres. Gas: oxygen; heating rate: 10°C/min; mass of fibres: 24.1 mg.

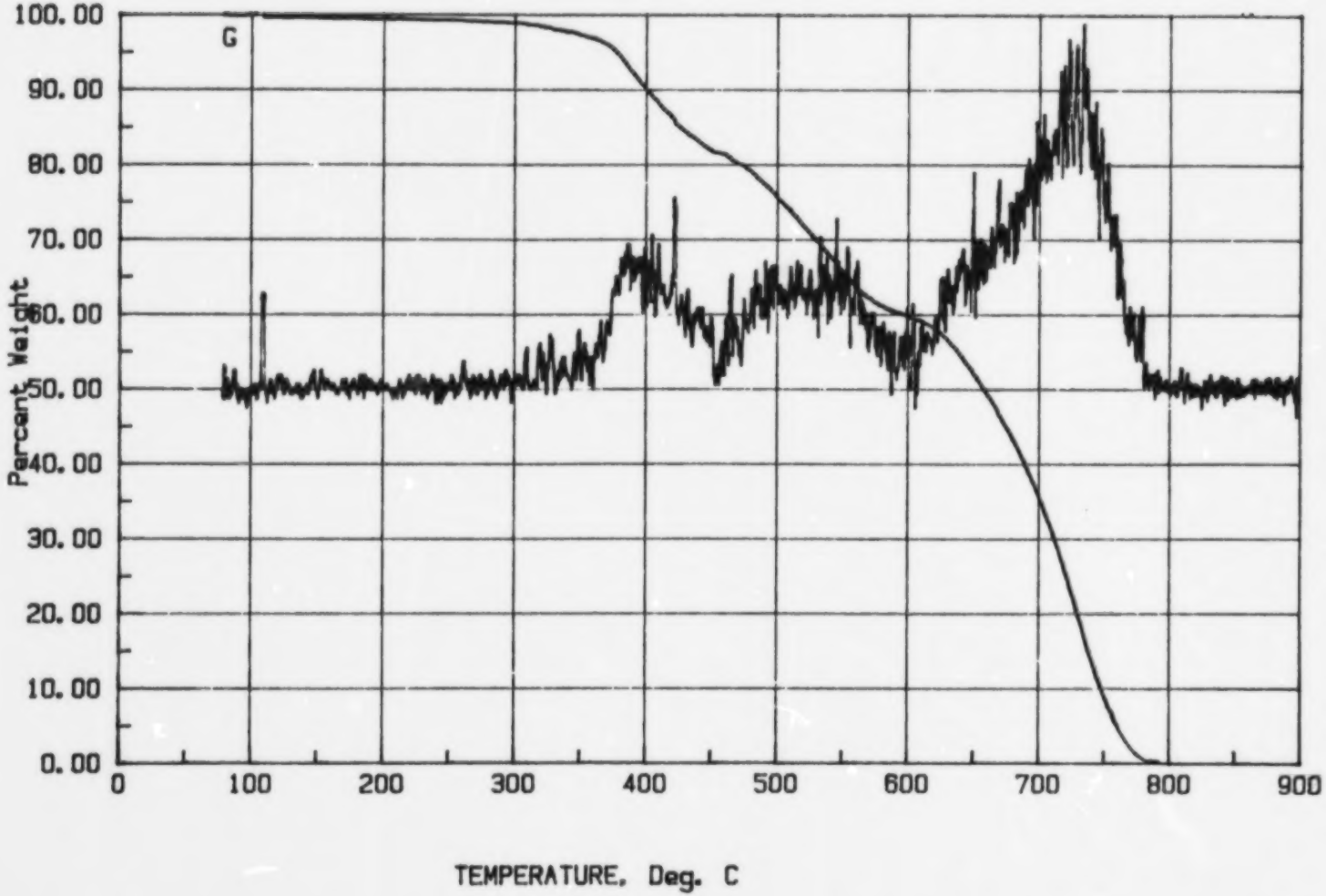


Figure 13. TG curve of Narmco 5208 prepreg. Gas: oxygen; heating rate: 10°C/min; mass of prepreg: 54.9 mg.

possible to find a temperature around 400 - 500°C which will allow isothermal decomposition of the epoxy resin without excessive oxidation of the graphite fibres.

The first experiment in isothermal mode was carried out at 500°C with the Narmco 5208 prepreg (batch #1103) and Figure 14 shows the variation of the sample weight and of the furnace temperature as a function of time. An inflexion point is observable at 80 minutes and corresponds to a loss of weight of about 40%. It is known that this composite has about this percentage of epoxy resin [26]. However, there is no stabilization of the weight of the sample as the time increases and this indicates a continuous oxidation of the graphite fibres. Thus, this temperature is too high to perform a well-defined isothermal decomposition of the epoxy prepreg.

The next experiment was done with the same prepreg at 460°C as shown in Figure 15. As in the previous case, the weight loss has not stabilized after three hours. The decomposition rate slows down when the weight loss is around 40%, but this temperature cannot give an accurate determination of the mass of the resin in the prepreg.

An experiment was done at 420°C with a synthetic epoxy-graphite prepreg. This was prepared by mixing short graphite fibres and neat Narmco 5208 epoxy resin (batch number 1023). The mixture contained 22.7 mg of graphite (34.8%) and 42.6 mg of resin (65.2%). The sample was maintained at 420°C for 7 hours and the curves are shown in Figure 16. As previously, the weight loss is not stable with time and this indicates oxidation of the graphite fibres. However, an enlargement of the last part of the curve (Figure 17) shows a small inflexion point at 280 minutes. This point corresponds to a weight loss of 66.5% and is probably caused by the disappearance of the epoxy resin followed by a faster oxidation of the graphite fibres. This percentage (66.5%) corresponds relatively well with the known percentage of resin (65.2%) but the difference is too large to use it to calculate accurate values of enthalpy. It is probable that due to the duration of the experiment, a significant percentage of graphite is oxidized, which increases the apparent percentage of resin found with the TG curve. Also, the inflexion point is extremely difficult to detect and the analysis time is too long to be practical.

It was observed in Figure 13 that there is an inflexion point at about 580°C which seems to correspond to the end of oxidation of the epoxy resin and to the beginning of oxidation of the graphite fibres. This point is near 40%, which is close to the expected value for the Narmco 5208 prepreg. Thus, some experiments were done with programmed temperature and well characterized prepregs in order to emphasize this inflexion point and to verify its relationship to the percentage of epoxy resin in the prepreg.

Four mixtures with known percentages of epoxy resin and graphite fibres were prepared and the TG curves were recorded up to 800°C in oxygen at a heating rate of

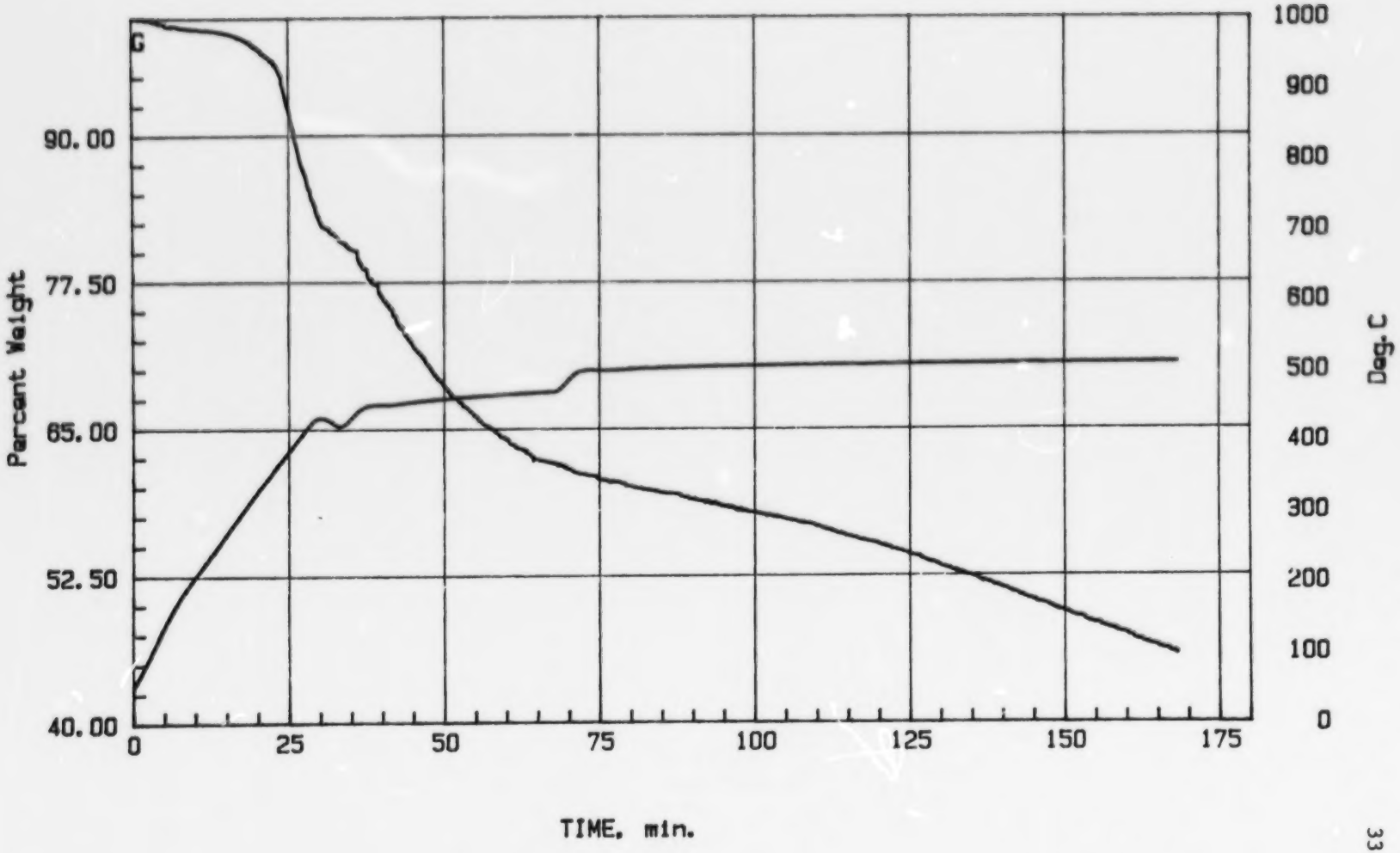


Figure 14. Isothermal TG curve of Narmco 5208 prepreg. Gas: oxygen; temperature: 500°C; mass of prepreg: 47.7 mg.

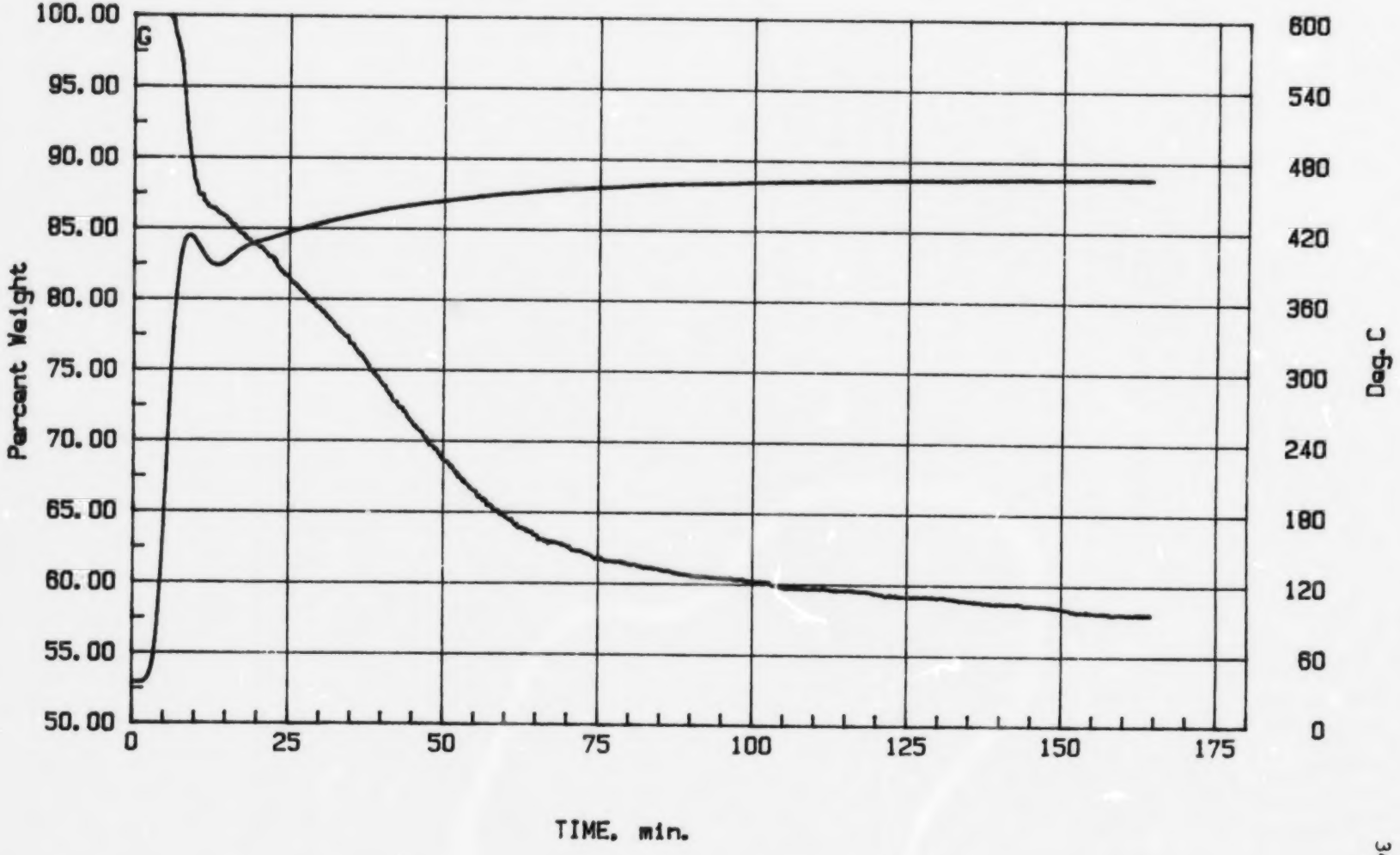


Figure 15. Isothermal TG curve of Narmco 5208 prepreg. Gas: oxygen; temperature: 460°C; mass of prepreg: 40.0 mg.

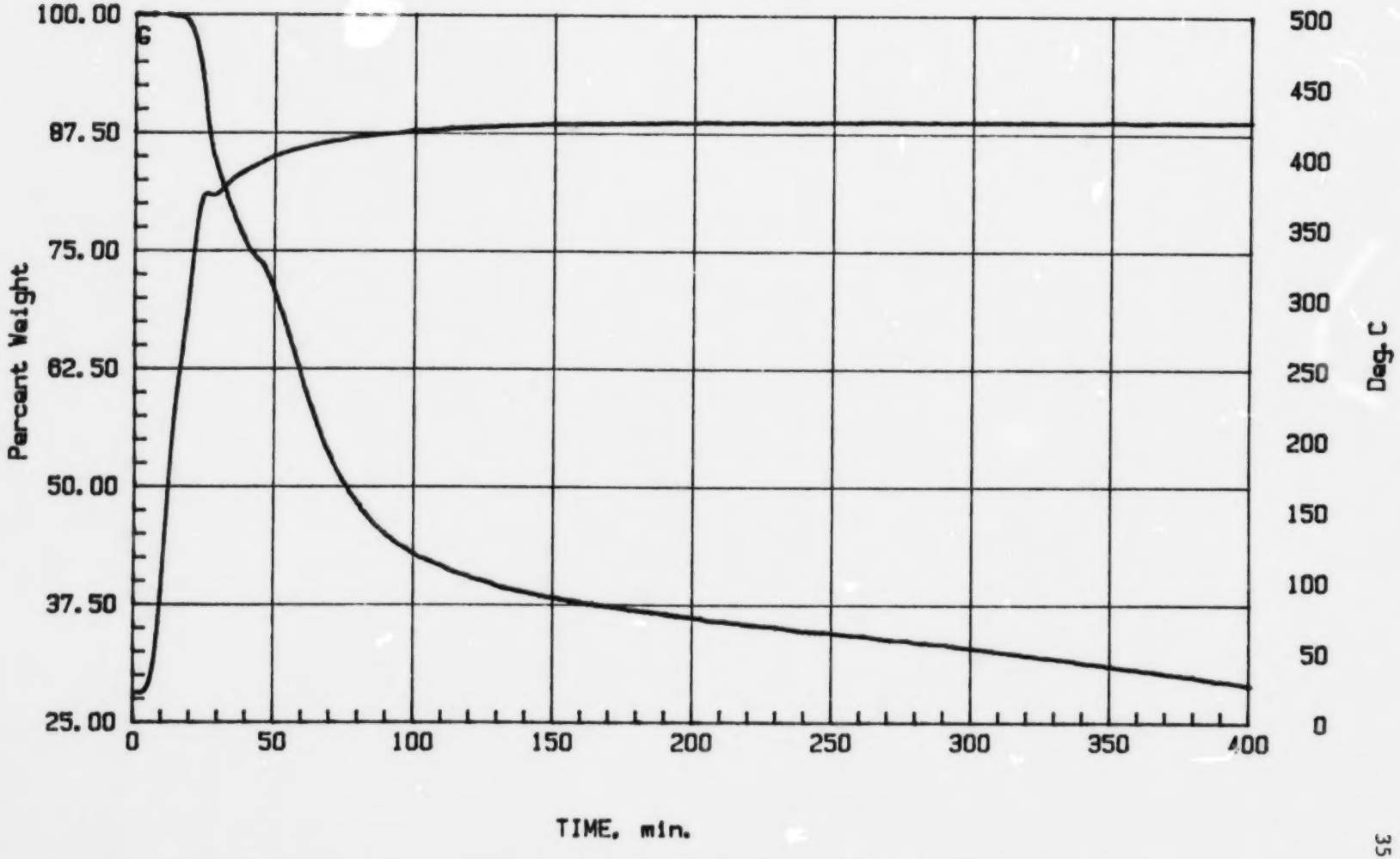


Figure 16. Isothermal TG curve of a prepared mixture of epoxy resin (65.2% w/w) and graphite fibres (34.8% w/w). Gas: oxygen; temperature: 420°C; mass of sample: 65.3 mg.

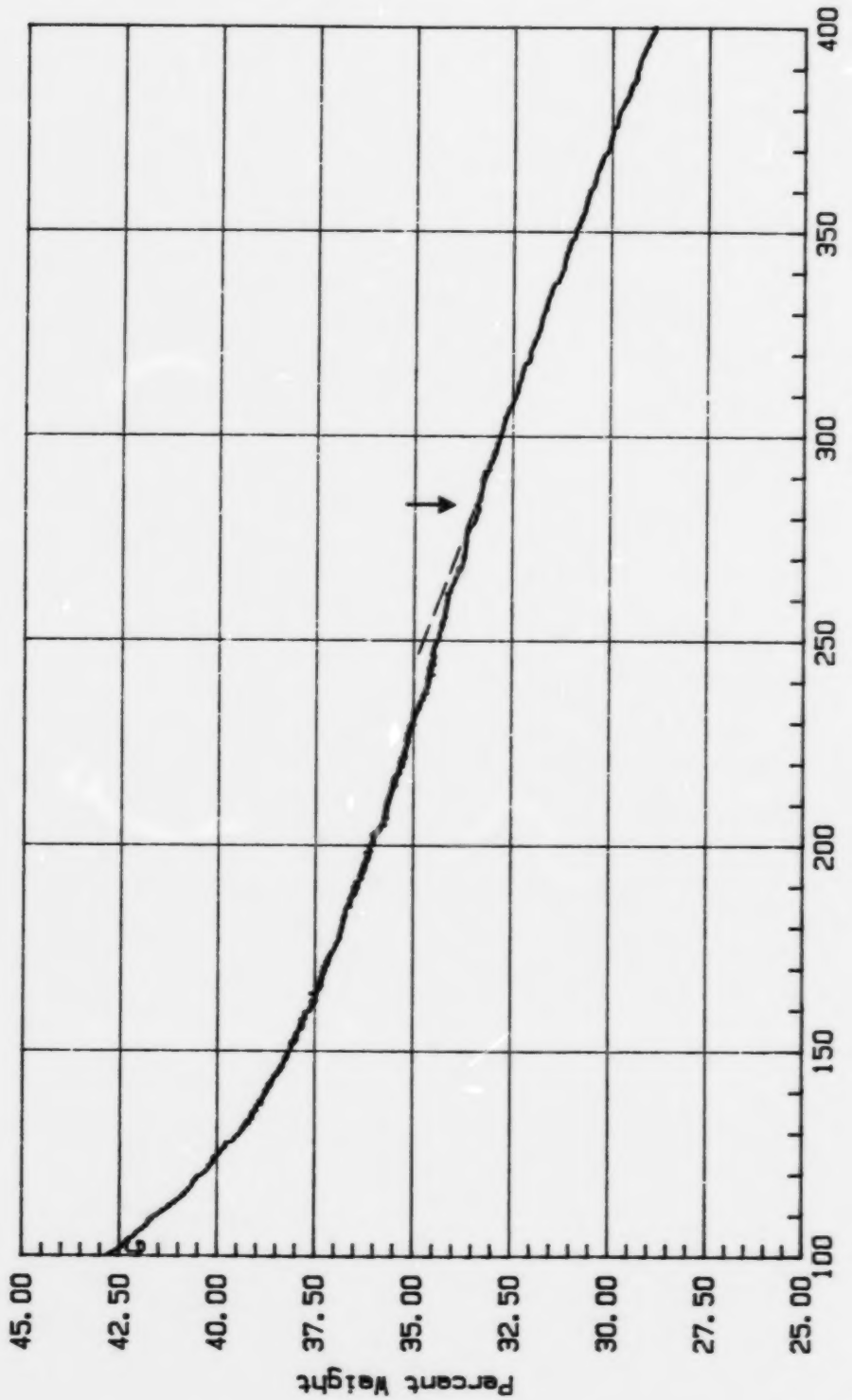


Figure 17. Enlarged area of Figure 16.

10°C/min. An example of a typical thermogram is given in Figure 18. The curve is similar to that of Figure 13. The inflexion point corresponding to the end of oxidation of the epoxy resin and to the beginning of oxidation of graphite fibres is observable at about 565°C (point 3). This section of the TG curve is enlarged in Figure 19. In addition to this point, the inflexion points labelled point 1 and point 2 in Figure 11 have been used to evaluate the percentage of resin. For these latter points, the values found on the TG curve are divided by the values found with the neat epoxy resin (51.8% and 47.6%). Table 4 summarizes the results obtained with the prepared mixtures of epoxy resin and graphite fibres.

Table 4. Thermogravimetric results obtained with known mixtures of epoxy resin and graphite fibres.

Mixture preparation data			TGA experimental results		
Mass graphite (mg)	Mass resin (mg)	% resin	% resin (point 1)	% resin (point 2)	% resin (point 3)
22.5	15.2	40.3	36.8	36.5	40.2
19.2	30.9	61.7	57.8	56.6	61.6
13.7	6.4	31.8	27.7	29.7	32.0
37.3	28.4	43.2	39.7	38.6	43.3

Clearly, only the inflexion point 3 allows a direct determination of the mass of resin in the sample. Thus, this point will be used for subsequent analyses.

The relative error of the mass determined at point 3 is evaluated as about 0.5%. For a typical value of 20 mg, the error is 0.1 mg. Thus, the mass determined with oxygen is more precise than the mass calculated from the isothermal experiment with nitrogen. The results in Table 4 demonstrate that this thermogravimetric determination of the mass of the resin in a prepreg is excellent and can be used to evaluate accurately the curing enthalpy of the epoxy resin.

Figure 20 compares the TG curves of a prepreg (batch #1103) and of a synthetic mixture (40.3% resin). The inflexion point is displaced by about 25°C towards higher temperature for the prepreg. This variation is explained by a better coverage of graphite fibres in the prepreg than in the prepared mixture and also by the different form of the sample. It is well known that a sample with a low ratio of surface area to mass will often

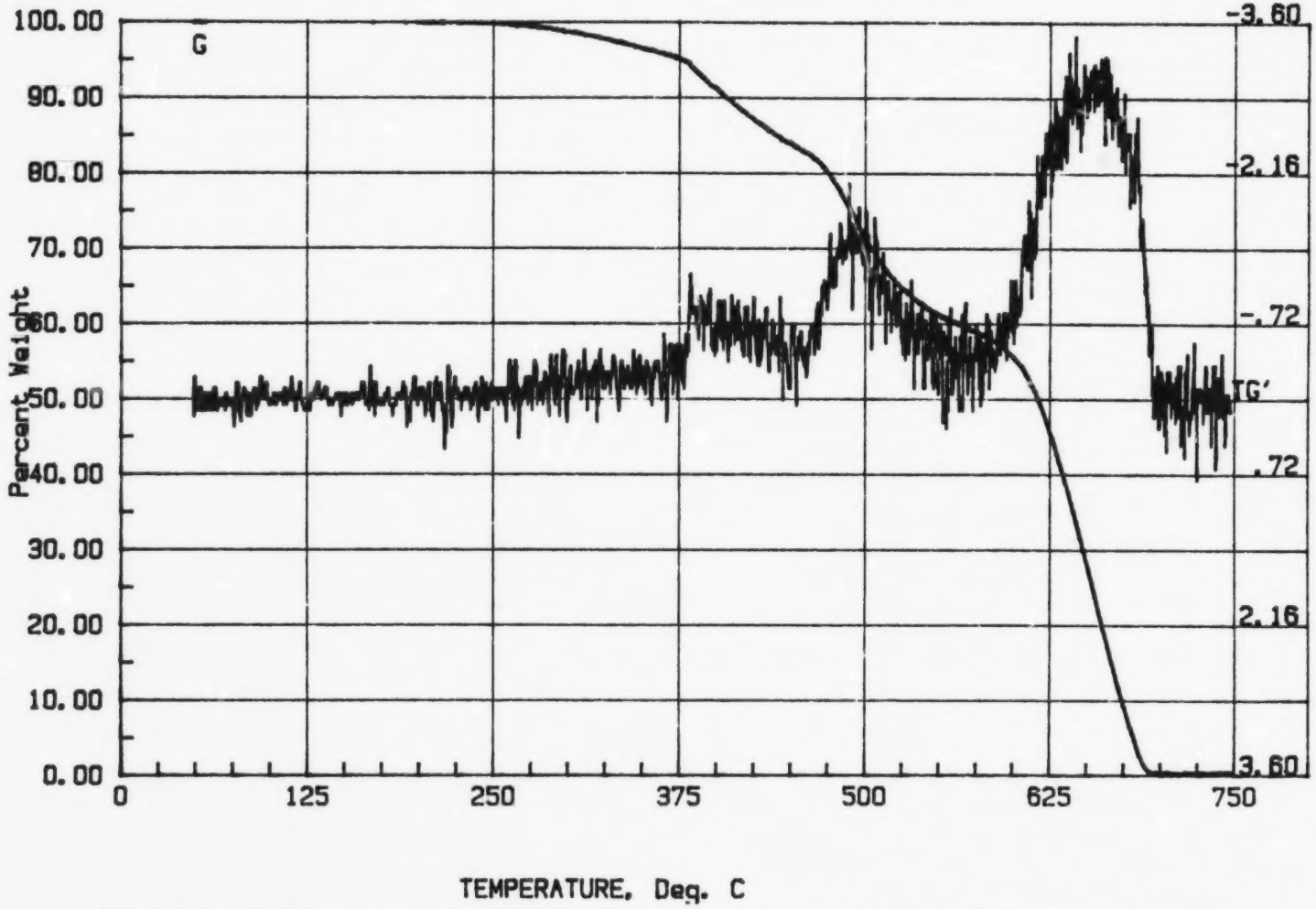


Figure 18. TG curve of a prepared mixture of epoxy resin (40.3% w/w) and graphite fibres (59.7% w/w). Gas: oxygen; heating rate: 10°C/min; mass of sample: 37.7 mg.

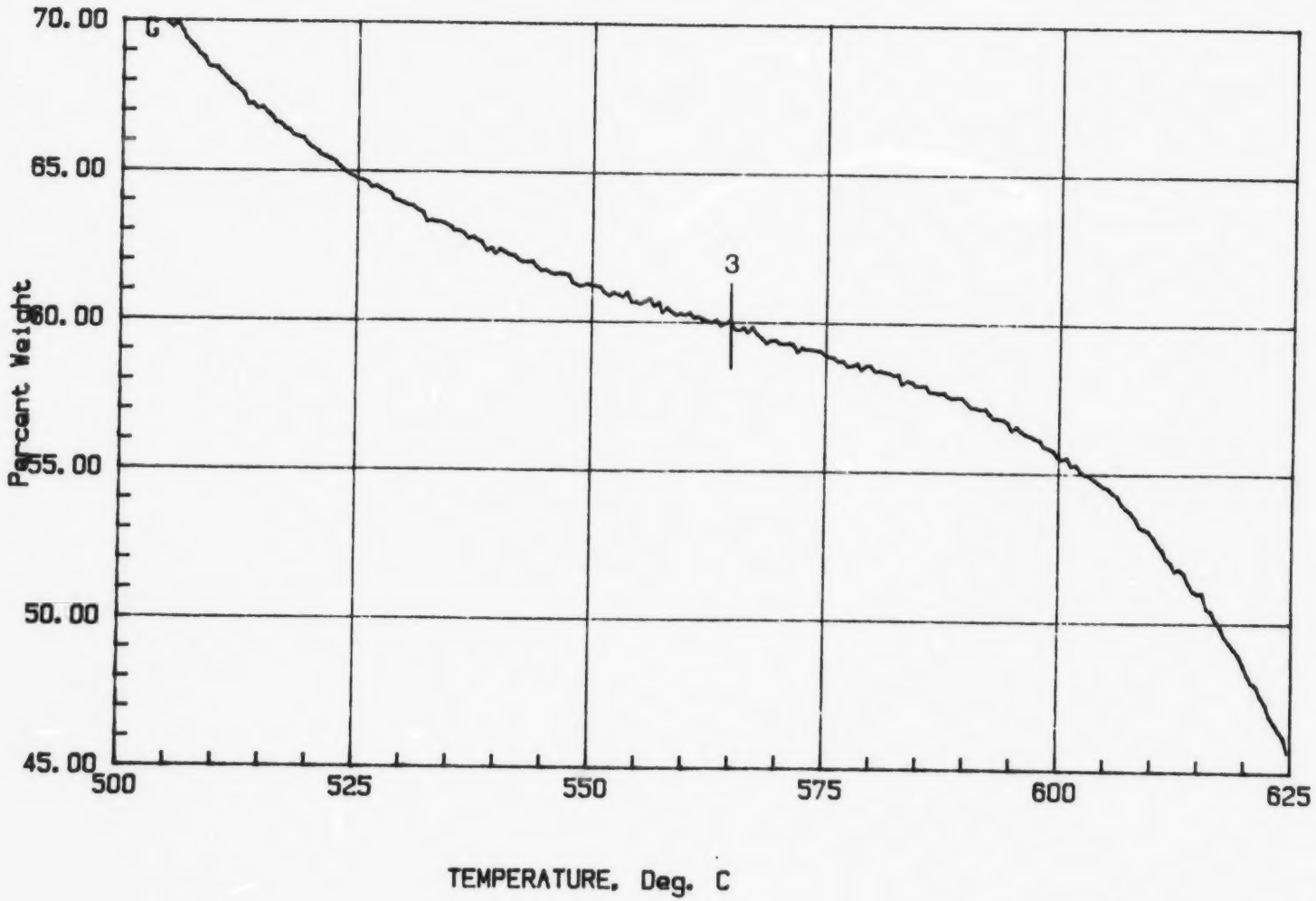


Figure 19. Enlarged area of Figure 18.

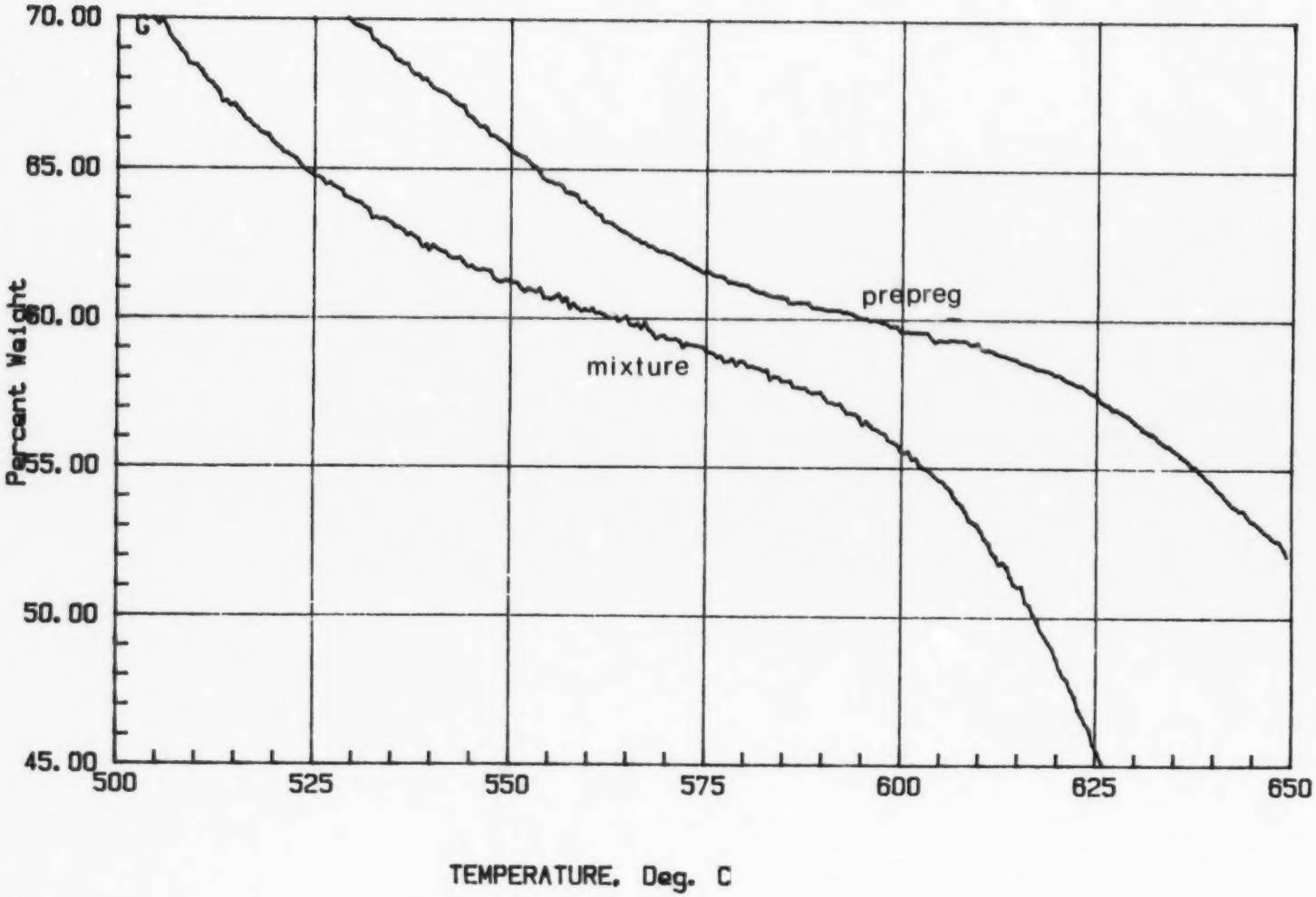


Figure 20. Comparison of TG curves of the prepared mixture of epoxy resin and graphite fibres and of the Narmco 5208 prepreg.

decompose more slowly than a sample of equal mass but consisting of very small particles [31]. As the prepreg is more dense and compact than the prepared mixture, it is reasonable to assume that the decomposition will be slower with the prepreg.

A comparison of the TG curve of graphite fibres (Figure 12) with Figure 20 indicates a possible percentage of oxidation of the graphite of about 4% for the synthetic mixture (565°C) and about 15% (590°C) for the epoxy-graphite prepreg. For the prepared mixtures, the determination of the percentage of resin is not affected by an eventual oxidation of the graphite fibres. However, for the prepreg, the percentage of oxidation can reach 15% and the possibility of decomposition of the graphite where the resin is thinner is perhaps not negligible. The percentage of resin in the composite for different samples from various batches ranges from 40 to 47% as shown in Table 5 (Section 2.3.2.2). These values are similar to those found using an organic liquid extraction [26]. It is assumed that a significant oxidation of the graphite fibres would increase the apparent percentage of resin found in the prepreg. Thus, it is believed that the determination of the mass of resin in a prepreg is not significantly modified by the oxidation of graphite and the inflexion point (point 3) corresponds to the end of decomposition of the epoxy resin and to the beginning of oxidation of the graphite fibres.

2.3.1.3 Air atmosphere

An experiment was done with air as atmosphere in order to check whether this environment is sufficiently oxidizing to decompose the epoxy-graphite prepreg in three well-defined steps. The resulting TG curve and its derivative are shown in Figure 21. A comparison with Figure 13 clearly shows that the inflexion point detected at 590°C in oxygen is not observed on the TG curve obtained in air. It is probable that with air as atmosphere the supply of oxygen is not sufficient to rapidly decompose the resin. Since this results in different kinetics of decomposition compared to a pure oxygen atmosphere, the use of air instead of oxygen as atmosphere is not suitable for accurate determination of the mass of resin in the prepreg.

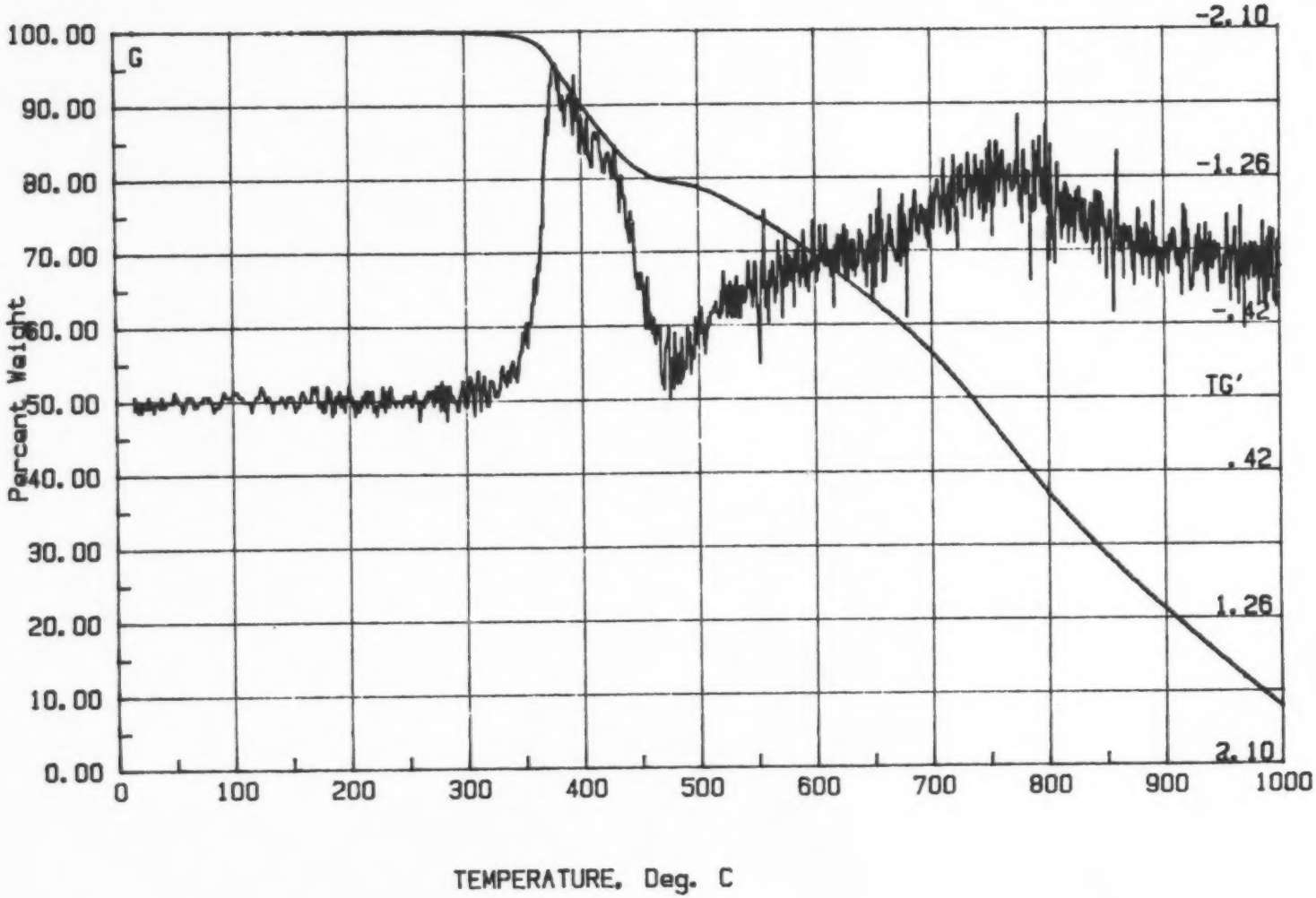


Figure 21. TG curve of Narmco 5208 prepreg. Gas: air; heating rate: 10°C/min; mass of prepreg: 63.5 mg.

2.3.2 Differential Scanning Calorimetry

2.3.2.1 Optimization

Various experimental factors such as atmosphere, heating rate, weight error and area error can affect the reproducibility in DSC. Chen and Hunter [25] have shown that the variation in the determination of the enthalpy of polymerization for the neat epoxy resin Narmco 5208 is substantial without an optimized experimental procedure. The sampling of a piece of prepreg causes a large error in the evaluation of ΔH [32]. Morgan et al. found that the reproducibility for ΔH is better than 5% for samples taken in close proximity (<10 cm apart) in a prepreg lot. However, the relative standard deviation increases to 30% for samples taken from the same lot but separated by a distance greater than 20 cm, or for samples taken from different lots.

In addition, Narmco 5208 epoxy resin starts to decompose at a fairly low temperature and low-molecular-weight compounds are released during heating [33]. Propenal has been positively identified as a thermal decomposition product. Many other aldehydes are also formed during the curing or during the heating of the cured resin. This fact has been confirmed by TGA and DSC. Figure 22 illustrates the TG curve up to 320°C of epoxy-graphite prepreg (batch #1014) with oxygen as atmosphere. This temperature (320°C) represents the upper limit for a DSC experiment, and it is seen that significant decomposition of the resin occurs within this range. Figure 23 shows the DSC curve of the same prepreg obtained in static air. After curing, decomposition of the resin prevents the signal from returning to its level before curing. Thus, the determination of the enthalpy of the curing reaction is affected to some extent by decomposition reactions. It is important to minimize these reactions in order to obtain accurate DSC results.

Assuming that oxidation of the resin is an important part of the degradation reactions, the use of nitrogen as atmospheric gas during the DSC experiments can significantly reduce these reactions. Figure 24 shows a thermogravimetric curve of Narmco 5208 prepreg (batch #1014) determined with nitrogen as atmosphere. A loss of weight corresponding to 1% is observed in the first part of the curve. This loss is attributed to the release of additives or impurities such as acetone [18] or methyl ethyl ketone [33]. Thermal degradation of the epoxy resin begins at 280°C. As the calculation of enthalpy from the DSC curve is usually done between 130°C and 273°C, it is assumed that the ΔH determined with nitrogen is almost totally related to the curing reaction between epoxy and hardener. Figure 25 illustrates the DSC curve of the prepreg obtained under

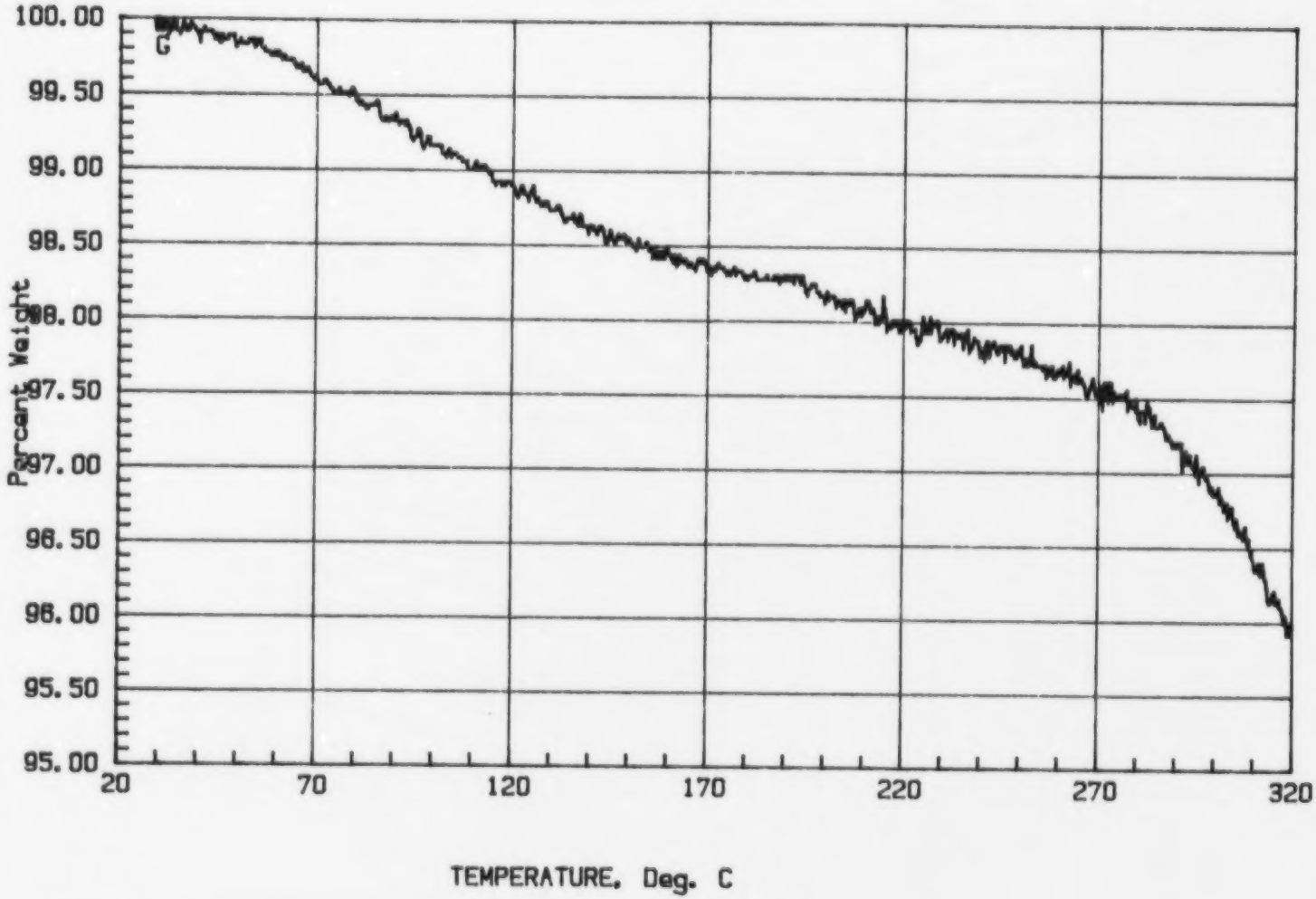


Figure 22. TG curve of Narmco 5208 prepreg. Gas: oxygen; heating rate: 10°C/min; mass of prepreg: 37.2 mg.

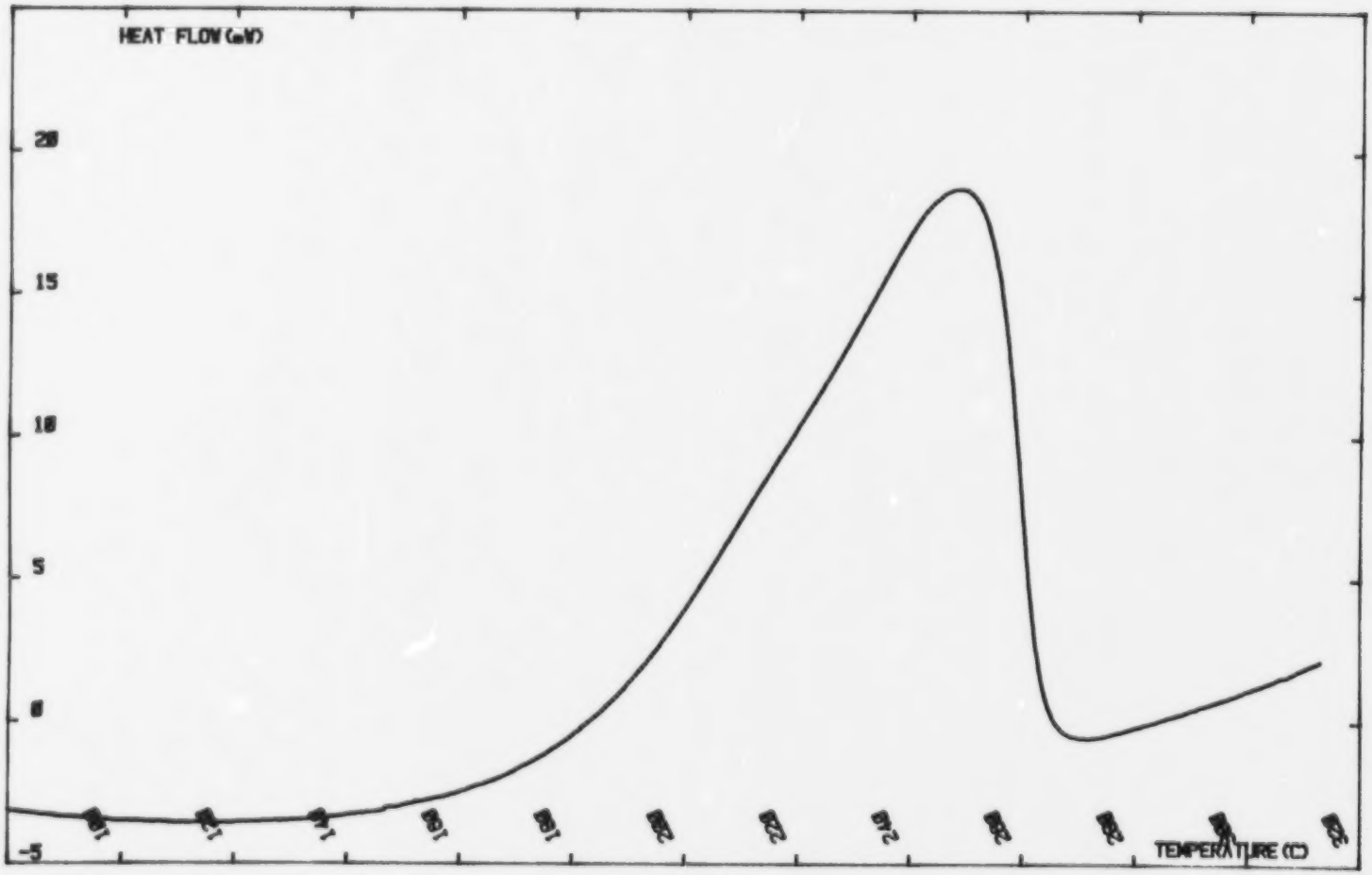


Figure 23. DSC curve of Narmco 5208 prepreg. Gas: oxygen; heating rate: 5°C/min.

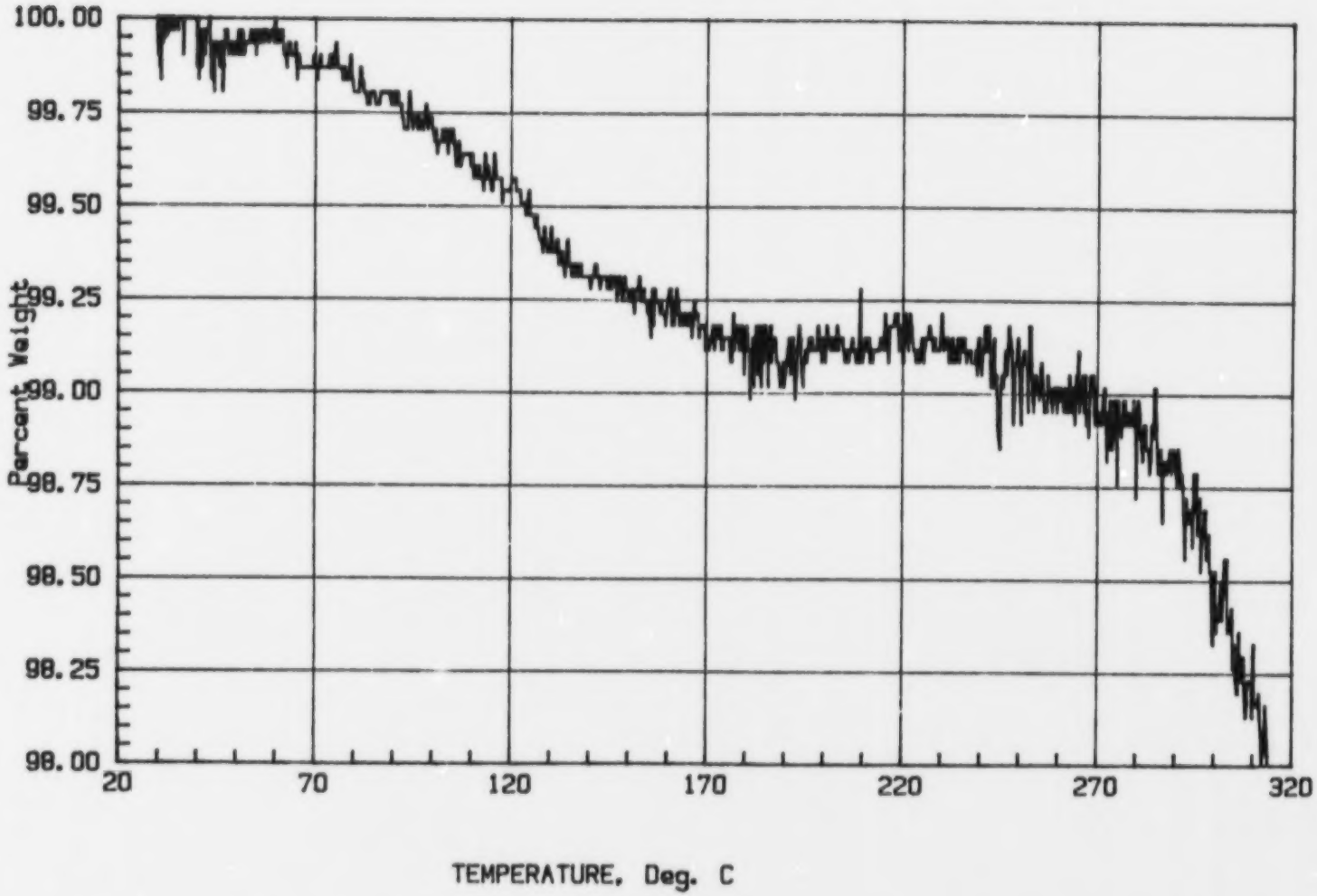


Figure 24. TG curve of Narmco 5208 prepreg. Gas: nitrogen; heating rate: 10°C/min; mass of prepreg: 30.5 mg.

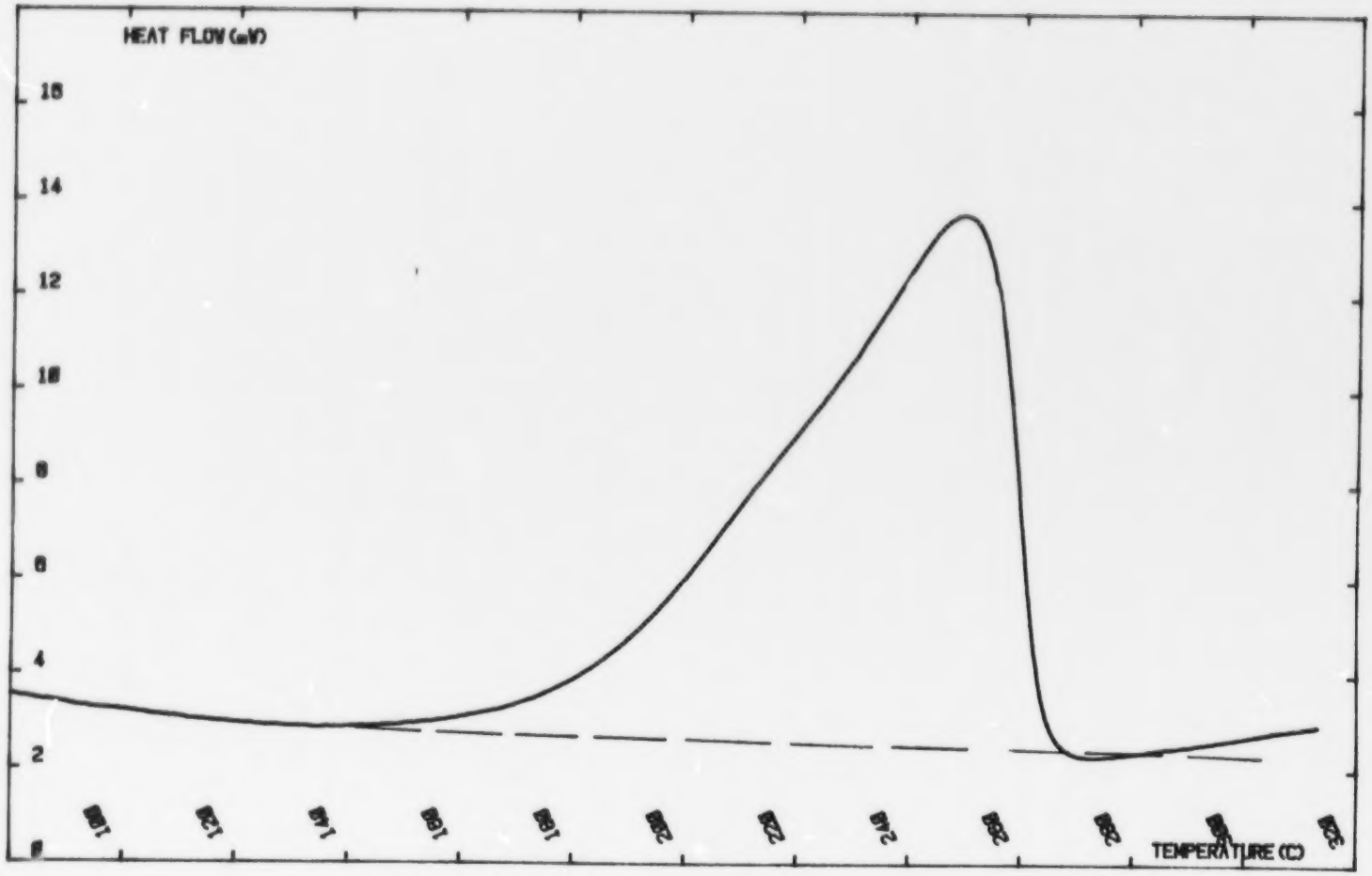


Figure 25. DSC curve of Narmco 5208 prepreg. Gas: nitrogen; heating rate: 5°C/min.

nitrogen, together with the baseline obtained using empty crucibles. The signal of the calorimeter returns to its initial level after the curing of the resin.

In addition to the nitrogen atmosphere, it is important to use two paired crucibles in the calorimeter in order to obtain a stable baseline without curvature. These prerequisites are necessary to obtain reproducible values of enthalpy.

2.3.2.2 Comparison of different batches of Narmco 5208

Several batches of Narmco 5208/WC3000 prepreg and neat resin were studied by dynamic DSC at a heating rate of 5°C/min with nitrogen as atmosphere. Samples were analyzed vertically in platinum cups. Thermograms for all the prepregs are similar to the curve given in Figure 25. After the DSC experiment, each sample was analyzed by thermogravimetry at a heating rate of 10°C/min with oxygen as atmosphere. Table 5 summarizes the results.

Table 5. DSC results for different batches of Narmco 5208/WC3000 prepreg.

#	Batch	Weight loss DSC %	% Resin	ΔH uncorrected (J/g)	ΔH corrected (J/g)
1	1014	2.2	44.6	581	548
2	1014	1.2	40.0	526	552
3	1014	2.7	42.8	555	545
4	1103	3.2	40.4	517	536
5	1103	2.9	42.0	517	517
6	1010	2.8	47.0	614	548
7	1010	4.3	42.5	548	542
8	1101	3.7	43.6	567	546
9	1101	4.3	44.5	588	555
10	1104	4.2	40.5	524	544
11	1104	3.5	40.1	526	551
12	1023	---	100.0	---	568
13	1023	---	100.0	---	563
14	1047	---	100.0	---	620
15	1047	---	100.0	---	612

During DSC, some volatile products are released and the percentage of weight lost during the experiment is given in the third column. This quantity is added to the amount of resin found by TGA to give the total resin content of the sample in question (column 4). The heat of reaction measured by DSC is then divided by the true resin weight to give the "corrected" enthalpy ΔH in joules per gram of resin (column 6). The "uncorrected" enthalpy values (column 5) were calculated using the nominal resin content of 42% for all samples.

Temperatures at the maximum of the DSC peak are extremely stable and vary slightly between 248 and 250°C. The enthalpy values were calculated by integrating the DSC peak between 130 and 273°C.

For three specimens from batch #1014, the mean uncorrected enthalpy is 554 J/g, with a standard deviation of 28 (5.0%), whereas the mean for the corrected enthalpy is 548 J/g with a standard deviation of 4 (0.6%). These results are in concordance with those reported by Morgan [32] who noted that an enthalpy variation of 5% is observed in the analysis of prepregs if samples are taken in close proximity on a lot. This was the case in our experiments. However, the correction using the exact mass of resin gives a relative standard deviation smaller than 1%.

If the percentage of resin in the prepreg is similar for two samples, the values of enthalpy are relatively reproducible even without correction. For example, this is observed for batches #1103 and #1104 in Table 5. However, if the percentage of resin in the prepreg varies significantly, the determination of the enthalpy without correction fails to give reproducible values and in these cases, the correction for the mass of resin gives better results (batches #1014 and #1010).

A decrease of enthalpy indicates an advancement of the curing reaction. The different batches may be arranged in the following order: 1047 > 1023 > 1101 ~ 1014 ~ 1104 ~ 1010 > 1103. The enthalpy for the two samples of neat epoxy resin (batches #1047 and #1023) is somewhat larger than for the prepreg. There are two possible explanations for this. Firstly, the impregnation process usually involves heating, thereby causing some advancement of the epoxy resin. Secondly, it has been reported [34] that the presence of reinforcing fibres (in that particular case, glass) in the resin affects the cure kinetics and gives a lower enthalpy of cure.

In reverse-phase liquid chromatography [19], using the peak corresponding to the reaction product, the order for the different batches was the following: 1047 < 1104 < 1103 ~ 1014 < 1101 ~ 1010 < 1023. This arrangement is somewhat different from that found with DSC. In comparison, the order found in infrared spectroscopy (ATR) using the multiple epoxy index (1047 > 1101 > 1014 ~ 1010 > 1104 > 1103) corresponds fairly well

to the DSC order.

In both DSC and ATR, the final result is a global measurement over all molecules containing epoxy groups, whereas in RPLC the order of advancement is determined from a specific compound without taking into consideration the influence of other compounds. The good agreement between DSC and ATR suggests that infrared spectroscopy could possibly be used as a faster method to evaluate the degree of advancement.

2.4 CONCLUSIONS

A dynamic thermogravimetric method has been developed with oxygen as atmosphere in order to accurately determine the percentage of resin in an epoxy-graphite prepreg. The inflexion point corresponding to the end of oxidation of the epoxy resin and to the beginning of oxidation of the graphite fibres is used to directly evaluate the mass of resin in the sample used. This quantity is then used in combination with differential scanning calorimetry results to calculate the enthalpy of the curing reaction in an epoxy resin. Reproducible values of enthalpy can be obtained in DSC if the thermogram is measured under a nitrogen atmosphere and the mass of resin is calculated via a TG curve. This method is an excellent application for a combined TGA-DSC instrument since the many manipulations leading to weight errors can be reduced and substantial savings in time can be achieved.

3. RECOMMENDED METHODS

3.1 PYROLYSIS - GAS CHROMATOGRAPHY

(1) With clean scissors, cut a small piece of the prepreg and weigh it using a microbalance. The mass of the sample should be between 0.5 and 1.0 mg.

(2) Put the sample in the center of a 20 mm long quartz tube and place the tube in the probe.

(3) When the desired experimental conditions are obtained, put the probe in the pyrolyzer interface installed at the head of the chromatographic column.

(4) Suggested experimental conditions:

Temperature of the pyrolyzer interface: 200 °C.
Flow rate of helium in the interface: 150 mL/min.
Pyrolysis temperature: 650 °C.
Duration of the pyrolysis: 10 s.
Capillary column: DB-17, 30 m x 0.259 mm, film thickness 0.25 µm.
Column temperature program: 50°C to 60°C (2°C/min)
and 60°C to 250°C (10°C/min)
Flow rate of helium in column: 1.5 mL/min.
Injector temperature: 250°C.
Detector: flame ionization detector (250°C).

(5) The areas of selected peaks are ratioed against the peak area of aniline (peak #2 of Figure 5). Peaks 3, 4, and 7 are the best indicators of the degree of cure of the prepreg. The ratio of aniline to phenol (peak #2 to peak #1) is a measure of the hardener/epoxy ratio.

3.2 THERMAL ANALYSIS

(1) With clean scissors, cut a small piece of the prepreg (3 mm x 20 mm).

(2) Put the sample in a platinum crucible and weigh. The mass of the sample must be between 30 and 40 mg.

(3) Record the thermogram at a heating rate of 5°C/min between 40°C and 320°C. Nitrogen is used as atmosphere and an empty platinum crucible is used as reference.

(4) Calculate the enthalpy by measuring the area under the DSC curve between 130°C and 273°C.

(5) Weigh the crucible with the prepreg in order to determine the loss of resin during the DSC experiment.

(6) Transfer the same sample to the thermobalance and record a TG curve from room temperature to 800°C at a heating rate of 10°C/min using oxygen as atmosphere.

(7) The mass of resin is obtained at the inflexion point on the TG curve at about 590°C as shown in Figure 19.

(8) The mass found by TG is added to the mass lost during the DSC experiment and the sum is taken as the total resin mass and used to calculate the exact enthalpy of curing.

4. REFERENCES

(1) S.A.Liebman, T.P.Wampler, E.J.Levy
Developments in pyrolysis capillary GC.
HRC CC J.High Resolut. Chromatogr. Chromatogr.Commun. **7**: 172-184 (1984)

(2) S.T.Jones
Applications of pyrolysis gas chromatography in an industrial research laboratory.
Analyst (London) **109**: 823-828 (1984)

(3) C.G.Smith
Practical analytical pyrolysis applications for the polymer industry.
Ch. 14 (p. 428) in Analytical Pyrolysis, K.J.Voorheers (Ed), Butterworths, London, 1984

(4) S.A.Liebman, D.H.Starnes, F.C.Schilling
Short-chain branching in PE and PVC using PHGC and C^{13} FTNMR.
J.Macromol.Sci., Part A **17**: 935 (1982)

(5) S.Tsuge, H.Ohtani
Pyrolysis - gas chromatographic studies on the microstructures of stereospecific polypropylenes.
Ch. 13 (p. 407) in Analytical Pyrolysis, K.J.Voorheers (Ed), Butterworths, London, 1984

(6) J.Q.Walker
Pyrolysis gas chromatographic correlation trials of the American Society for Testing and Materials.
J.Chromatogr.Sci. **15**: 267 (1977)

(7) E.J.Levy, J.Q.Walker
The model molecular thermometer: a standardization method for pyrolysis gas chromatography
J.Chromatogr.Sci. **22**: 49 (1984)

(8) K.C.Cole, D.Noël, J.-J.Hechler
New developments in physicochemical characterization of high-performance epoxy-graphite composites
Nat. SAMPE Symp. Exhib. [Proc] **30**: 624 (1985)

(9) B.Maynard, J.E.Twichell, J.Q.Walker
Determination of carboxyl-terminated-butadiene-nitrile polymer in commercial cresol novalac epoxy resin systems by pyrolysis capillary gas chromatography and mass spectrometry.
J.Chromatogr.Sci. **17**: 82-86 (1979)

(10) J.G.Moncur, A.B.Campa, P.C.Pinoli
Analysis of aerospace adhesives and prepreg composites fabrics.
HRC CC J.High Resolut. Chromatogr.Chromatogr.Commun. **5**: 322-324 (1982)

(11) J.E.Williamson, M.J.Cocksedge, N.Evans
Analysis of polyurethane and epoxy based materials by pyrolysis-mass spectrometry.
J.Anal.Appl. Pyrolysis **2**: 195-205 (1980)

(12) I.F.Lindgren
Quantitative analysis of some cured epoxy composites.
Nat. SAMPE Symp. Exhib. [Proc] **29**: 1395 (1984)

(13) F.Farré-Rius, G.Guiochon
On the conditions of flash pyrolysis of polymers as used in pyrolysis - gas chromatography.
Anal.Chem. **40**: 998 (1968)

(14) H.S.Chu, J.C.Seferis
Dynamic mechanical experiments for probing process-structure-property relations in amine-cured epoxies.
Polym. Compos. **5**: 124 (1984)

(15) P.R.Griffiths, J.A. de Haseth, L.V.Azarraga
Capillary GC/FTIR.
Anal.Chem. **55**: 1361A (1983)

(16) L.S.Ettre, J.L.DiCesare
GC using very thick film capillary columns.
Am. Lab. (Fairfield, Conn.) **16**: 76 (1984)

(17) K.C. Cole, D. Noël
Physicochemical characterization of high-performance fibre-reinforced organic-matrix composites. Part 1. General discussion and literature review.
Report IGM 86-101-307, National Research Council Canada Publication 25839, May 1986.

(18) K.C. Cole, D. Noël
Physicochemical characterization of high-performance fibre-reinforced organic-matrix composites. Part 2. Applications of infrared spectroscopy.
Report IGM 86-101-321, National Research Council Canada Publication 26034, June 1986.

(19) D. Noël, K.C. Cole
Physicochemical characterization of high-performance fibre-reinforced organic-matrix composites. Part 3. Applications of liquid chromatography.
Report IGM 86-101-424, National Research Council Canada Publication 26579, September 1986.

(20) J. Sickfeld, W. Mielke
Application of thermal analysis for the investigation of epoxy resins.
Prog. Org. Coat. **12**: 27-116 (1984)

(21) E.A. Turi (Ed.)
Thermal Characterization of Polymeric Materials
Academic Press, New York, 1981

(22) R.C. Mackenzie
Nomenclature in thermal analysis. Part IV.
Thermochimica Acta **28**: 1-6 (1979)

(23) M. Cizmeciogly, A. Gupta
Cure kinetics of epoxy matrix resin by differential scanning calorimetry.
SAMPE Quarterly, April 1982, pp 16-20

(24) E.B. Stark, A.M. Ibrahim, J.C. Seferis
The effect of bisphenol A Novolac resin on high-performance epoxy formulations.
Chapter in "Interrelations between processing, structure, and properties of polymeric materials", J.C. Seferis & P.S. Theocaris (Eds.), Elsevier, 1984

(25) J.S. Chen, A.B. Hunter
Development of quality assurance methods for epoxy graphite prepreg.
Technical Report NASA-CR-3531 (1982); NTIS No N82-22318

(26) K.C. Cole, D. Noël
Physicochemical characterization of high-performance fibre-reinforced organic-matrix composites. Part 5. A study of the room-temperature aging of Narmco 5208/WC3000 prepreg.
National Research Council Canada Report, in preparation.

(27) R.L. Hassel, R.L. Blaine
Composite evaluation by thermal analysis.
Natl. SAMPE Symp [Proc] **24**: 342-349 (1979)

(28) J.C. Seferis
Polyetheretherketone (PEEK): processing, structure, and properties studies for matrix in high-performance composites.
Polym. Compos. **7**: 158-169 (1986)

(29) R.B. Prime
Thermosets.
Chapter in Thermal Characterization of Polymeric Materials, E.A. Turi (Ed), Academic Press, New York, 1981 (p.509)

(30) R. Schmid, M. Fisher
Thermoanalytical characterization of matrix resins and composites.
SAMPE - Materials and Process - 5th Technology Conference of the European Chapter, 1984, vol. 2, paper 18.

(31) W.W. Wendlandt
Thermal Analysis. 3rd Ed.
John Wiley & Sons, New York, 1986, pp.36-37.

(32) R.J. Morgan, C.M. Walkup, T.H. Hoheisel
Differential scanning calorimetry studies of the cure of carbon fiber-epoxy composite prepregs.
J. Appl. Polym. Sci. **30**: 289-296 (1985)

(33) M.A. Grayson, C.J. Wolf
Low-temperature thermal decomposition of an epoxy resin.
J. Polym. Sci., Polym. Chem. Ed. **22**: 1897-1907 (1984)

(34) J. Mijovic
Cure kinetics of neat versus reinforced epoxies.
J. Appl. Polym. Sci. **31**: 1177-1187 (1986)